PB89-233514

Proceedings: US/FRG (Federal Republic of Germany) Workshop on Photochemical Ozone Problem and Its Control US Experiences and the Situation in Europe

(U.S.) Environmental Protection Agency, Research Triangle Park, NC

Mar 89

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(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA/600/9-89/058	2.
3. RECIPIENT'S ACCESSION NO. PB89-233514/AS	
4. TITLE AND SUBTITLE PROCEEDINGS US/FRG WORKSHOP ON PHOTOCHEMICAL OZONE PROBLEM AND ITS CONTROL. US EXPERIENCES AND THE SITUATION IN EUROPE	5. REPORT DATE March 1989 6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) K. Becker, K. Demerjian, H. Jeffries, U. Schurath	8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM ELEMENT NO. 11. CONTRACT/GRANT NO.
12. SPONSORING AGENCY NAME AND ADDRESS Atmospheric Research & Exposure Assessment Lab.--RTP, NC Office of Research and Development U. S. Environmental Protection Agency Research Triangle Park, N. C. 27711	13. TYPE OF REPORT AND PERIOD COVERED 14. SPONSORING AGENCY CODE EPA/600/09
15. SUPPLEMENTARY NOTES	

16. ABSTRACT

Concern for the photochemical ozone problems in the US and Europe led the US and FRG Governments to organize and conduct the subject Workshop in May 1988, in Cologne, FRG, to review the magnitude of the problem, underlying science, and outstanding technical issues. Discussions focussed on the pervasiveness, cause/effect and control aspects of the problem. Issues and information gaps were identified in the atmospheric chemistry and transport and ozone modeling areas, and recommendations for future research activities were formulated including one for a 2nd Workshop to be conducted in the US.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

18. DISTRIBUTION STATEMENT RELEASE TO PUBLIC	19. SECURITY CLASS *(This Report)* UNCLASSIFIED	21. NO. OF PAGES 79
	20. SECURITY CLASS *(This page)* UNCLASSIFIED	22. PRICE A05

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

PB89-233514
EPA/600/9-89/058
March 1989

United States
Environmental Protection
Agency

Atmospheric Research and
Exposure Assessment Laboratory
Research Triangle Park NC 27711

Research and Development

EPA

Proceedings US/FRG Workshop on Photochemical Ozone Problem and Its Control— US Experiences and the Situation in Europe

REPRODUCED BY
U.S. DEPARTMENT OF COMMERCE
NATIONAL TECHNICAL INFORMATION SERVICE
SPRINGFIELD, VA. 22161

EPA/600/9-89/058
March 1989

PROCEEDINGS

US/FRG WORKSHOP

ON

PHOTOCHEMICAL OZONE PROBLEM AND ITS CONTROL.

US EXPERIENCES AND THE SITUATION IN EUROPE

May 4-6, 1988
Senats-Hotel
Cologne, FRG

WORKSHOP CO-CHAIRMEN

B. Dimitriades, US Environmental Protection Agency

D. Jost, Umweltbundesampt, FRG

STEERING COMMITTEE

K. Becker, FRG, Chairman
K. Demerjian, USA
H. Jeffries, USA
U. Schurath, FRG

Edited by

Basil Dimitriades
Atmospheric Research and Exposure Assessment Laboratory
Research Triangle Park, NC 27711
USA

DISCLAIMER

Although the workshop described in this report has been funded partially by the U. S. Environmental Protection Agency under contracts to invited participants, the report has not been subjected to the Agency's required peer and policy review and therefore does not necessarily reflect the views of the Agency and no official endorsement should be inferred. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

Printed in March 1989

by the

US Environmental Protection Agency

Research Triangle Park, NC 27711

USA

PREFACE

This Workshop was held within the framework of cooperation under the US-German Environmental Agreement. It contributes to high priority activities identified by Minister Toepfer and Administrator Thomas during their December 1987 meeting.

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WORKSHOP

THE PHOTOCHEMICAL OZONE PROBLEM AND ITS CONTROL

Senats-Hotel
Unter Goldschmied 9-17
Cologne, West Germany

May 4-6, 1988

A G E N D A

Wednesday, May 4, 1988, 9:00 AM - 6:00 PM

SESSION I: MAGNITUDE OF OZONE PROBLEM. TRENDS — Chairman: D. Jost, FRG

- Ozone and Precursor Emission Trends in the US — T. Curran, USA
- Concentrations of Ozone and Precursors in Germany — W. Fricke, FRG
- Ozone in Western Europe — K. Nodop, FRG
- Background Ozone. Levels, Trends, and Origins — K. Demerjian, USA
- Ozone Trends Within Large Metropolitan Areas. The Los Angeles Basin — T. McGuire, USA

L U N C H

SESSION II: ON-GOING CONTROL POLICIES — Chairman: B. Dimitriades, USA

- Ozone Control in Germany — E. Weber, FRG
- Ozone Control Policy in the U.S. — E. Meyer, USA
- Assessment of Effectiveness of NO_x Control as an Ozone Control Strategy — W. Sylte, USA
- On the Effectiveness of the USEPA Control Strategy for Ozone. An Opposing Viewpoint — H. Walker, USA

SESSION III:	ESTIMATES OF EMISSION DATA FOR VOC AND NO_X	Chairman:	H. Jeffries, USA
	- Problems with Existing Emission Inventory Data Bases		K. Schere, USA
	B R E A K		
	- Auto Emission Estimates. Current Improvements		F. Black, USA
	- European Inventory of Ozone Precursor Emissions		C. Veldt, NL
SESSION IV:	CHEMISTRY OF TROPOSPHERIC OZONE FORMATION	Chairman:	K. Becker, FRG
	- Recent Developments in O_3 Mechanism and Existing Issues		H. Jeffries, USA
	- The Chemistry of Ozone Formation Tested by Atmospheric OH Measurements		U. Platt, FRG
	- The Present Knowledge of Kinetic Data Important for Ozone Chemistry		A. Kerr, UK

7:00 PM Dinner hosted by Workshop Organizers

Thursday, May 5, 1988, 9:00 AM - 5:00 PM

SESSION V:	TRANSPORT/DISPERSION OF OZONE AND PRECURSORS	Chairman:	K. Demerjian, USA
	- Transport of Ozone by Airborne Measurements		D. Paffrath, FRG
	- Model Prediction of Transport and Dispersion		J. Pankrath/ I. Jacobsen, FRG
	- USEPA's Regional Ozone Model		K. Schere, USA
SESSION VI:	MODELING RESULTS ON OZONE FORMATION FROM PRECURSORS UNDER DIFFERENT CONDITIONS	Chairman:	H. Jeffries, USA
	- Effectiveness of Alternative Urban/ Regional Control Strategies for Ozone		E. Meyer/ J. Tikvart, USA
	- Assessment of Ozone-Related Controls in California Urban Areas		T. McGuire, USA

- Results from Modeling of Ozone Formation in Germany and Neighboring Countries — R. Stern, FRG

L U N C H

SESSION VII: VALIDATION OF MODEL PREDICTIONS. SENSITIVITY TO INPUT DATA/PARAMETERS — Chairman: U. Schurath, FRG

- Sensitivity Analysis of EKMA Input Parameters on VOC Control Requirements — H. Jeffries, USA
- Evaluation of USEPA Regional Oxidant Model in the North East US — K. Schere, USA
- Sensitivity Analysis of Model Predictions Upon Chemical Input Data — R. G. Derwent, UK

B R E A K

- Evaluation of Urban Airshed Models with Recent Field Measurements in NY — S. T. Rao, USA
- Effects of Different Wind Field Analyses on Airshed Model Predictions — R. Kessler, USA

5:00 PM Visit to Bayer Plant and hosted dinner

Friday, May 6, 1988, 9:00 AM - 5:00 PM

SESSION VIII: SUMMARY/CONCLUSIONS — Chairman: K. Becker, FRG; Co-Chairman: H. Jeffries, USA

- Discussions. End of Workshop.

L U N C H

- Steering Committee Meeting — Chairman: K. Becker, FRG

Saturday, May 7, 1988, 9:00 AM - As Needed

- Steering Committee Meeting — Chairman: K. Becker, FRG

Acknowledgement

The Workshop was organized at the instigation of Drs. Gary Foley (USA) and Erich Weber (FRG). The Workshop program and agenda were developed by Drs. Dimitriades and Becker. Workshop arrangements were made under Dr. Becker's direction. The Workshop report was prepared based on meeting presentations and on followup discussions by all Workshop participants under the guidance of the Workshop Steering Committee. Drs. Dimitriades, Demerjian, Curran, Derwent, Nodop, Fricke, Kley, Lübkert, Schere, Jeffries, Kerr, Kessler, Stern, Meyer, Walker, Sylte and McGuire prepared summary statements which were edited by Dr. Dimitriades into a structured report. The report was reviewed and finalized by the Steering Committee. Ms. K. Curtis and Ms. C. Morawa provided secretarial assistance for organization of the Workshop and preparation of the Proceedings report. The contributions of these named individuals and of all other Workshop participants are acknowledged with gratitude by the Workshop organizers.

PHOTOCHEMICAL OZONE PROBLEM AND ITS CONTROL. US EXPERIENCES AND THE SITUATION IN EUROPE

1.0 INTRODUCTION

The understanding of the significance of ozone occurrence in the troposphere can be viewed from three distinct points of view. First, ozone plays an important role in controlling the chemical composition of the troposphere as a result of being a major source of hydroxyl (HO) radicals. Second, ozone is a radiatively active gas which impacts the energy budget of the troposphere so as to cause global warming ("greenhouse effect"). And third, ozone has been found to cause adverse effects on human health, vegetation and materials[1]. Thus, ozone alone and with other pollutants synergistically irritate the respiratory system causing reduction in pulmonary function and increase susceptibility to infections and asthma attacks. Also, it reduces crop yields and growth and lifetime of trees, and damages rubber, paint, and other materials[1]. And finally, ozone and other oxidants have been found to instigate the formation of acid rain and the production in air of toxic pollutants such as formaldehyde and other mutagens.

There has been significant debate as to the quantitative details of the sources of ozone in the relatively clean free troposphere, but, in general, it is widely accepted that the major sources are the stratosphere and photochemical reactions of methane, carbon monoxide and nitrogen oxides (NO_x) (Figure 1-1). In the polluted tropospheres, however, that is, within the 1-2-Km boundary layer adjacent to the surface, ozone and other oxidant species are being formed mainly from photochemical reactions of non-methane volatile organics (NMVOC or in short VOC with respect to ozone formation, including also CO) and NO_x emissions associated with manmade activities (Figure 1-1). It is primarily this latter photochemical ozone arising from polluted atmospheres that is of interest and the subject of this report.

The photochemical ozone phenomenon has been studied extensively in the US and to some extent in Europe, Japan, Canada, and Australia also. These studies yielded a reasonably good--but not necessarily sufficient--understanding of the chemistry and meteorology underlying the photochemical ozone formation process and led to development of models capable of predicting photochemical ozone formation in time and space. In the US, where the photochemical ozone problem is most severe, laws have been enacted since 1970 that required the Federal and State Governments to promulgate emission control regulations sufficiently stringent to reduce ambient ozone concentrations down to the national ambient ozone air quality standard of 0.12 ppm (1-hour concentration not to be exceeded more than 1 day/year). Progressively more stringent emission and "equipment design" standards were promulgated during the 1970's and 1980's, which were intended to bring about reductions in emission levels that would more than offset the increases due to growth. Thus, VOC emissions were estimated to have decreased 19% during the 1977-86 period and NO_x emissions 8%. The improvement associated with automobile emissions was 39% for VOC and 13% for NO_x during that period and it occurred despite a 24% increase in vehicle kilometers of travel.

Processes Contributing to Tropospheric Ozone Budget

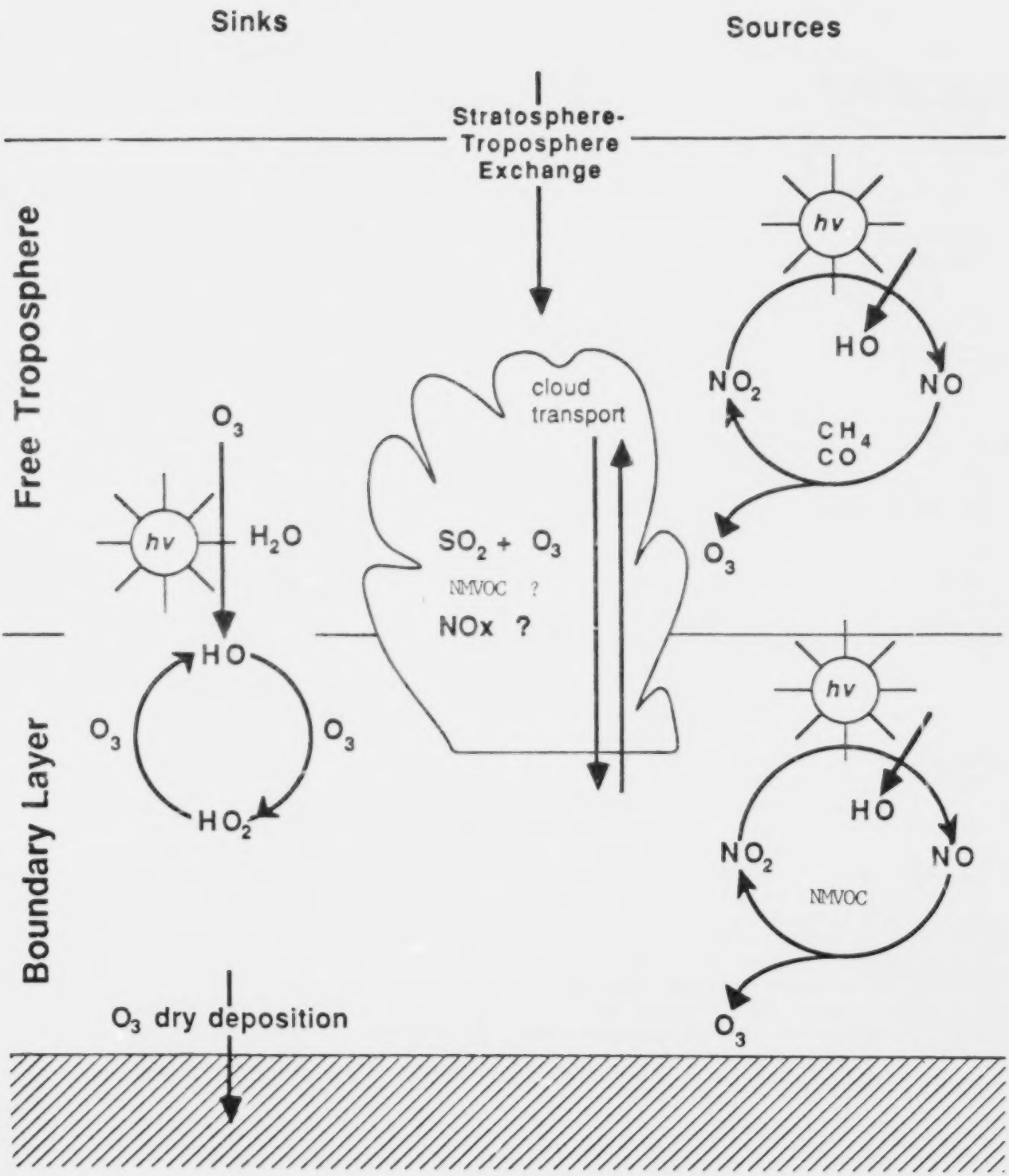


Figure 1-1

Despite such supposed emission reductions, however, and contrary to model predictions, the photochemical ozone problem in the US is still severe and very much of concern. While peak ozone concentrations, generally, have been reduced, there are still more than 60 "non-attainment" urban areas in the US, with some 75 million of people exposed to ambient ozone concentrations that exceed the air quality standard by as much as 0.23 ppm. The reasons for such persistence and pervasiveness of the ozone problem are not well understood.

This apparently inexplicable and disappointingly small success of the ozone control programs in the US raised some questions on the sufficiency of the current understanding of the ozone problem. Critics have gone as far as to allege that the US ozone control policies are grossly misdirected in being centered around unilateral control of the VOC precursor. However, a balanced view of the control program experience in the US would be that progress has been made but that more needs to be done. Initial control efforts emphasized VOC reductions but in some situations models may be used to evaluate the effectiveness of additional NO_x controls particularly in terms of the possible effect on population exposure. There is an awareness in the US that most of the large stationary sources are already controlled and that future controls on smaller sources will be expensive. For mobile sources, the USEPA has proposed onboard equipment on all new vehicles to control VOC emissions during refueling. Other possibilities being looked at include fuel volatility, stricter inspection and maintenance requirements, and the possible use of alternative fuels. Experience to date suggests that future reductions will be difficult and there are definite concerns about what an area such as Los Angeles would have to do to attain the US ozone standard.

Given the large socioeconomic penalties incurred by the ozone-related controls, the above uncertainties and doubts were disturbing and led USEPA to undertake an effort to re-examine and revise its ozone control policies. It is in this spirit of self-assessment that the USEPA agreed to participate in this Workshop and committed itself to present and discuss the US experiences and to expose its ozone control thinking and policies to the judgment of the international scientific community.

On its part, the FRG Government is concerned that the effects of photochemical ozone on human health and on the country's forest resources have grown in severity to the point that serious consideration must be given to commencing a control effort. The FRG Government is also keenly interested in assessing problems associated with the transport of ozone-related pollutants from or to neighboring countries. In the face of the questions raised by the US experience, however, and of the costs and political complications associated with even modest control measures, it is imperative that any control initiatives to be undertaken by the FRG (or the neighboring countries) be designed with the utmost care and confidence. The accuracy and completeness, therefore, of existing pertinent scientific evidence are the main subjects of interest to Germany and the primary reason for the German involvement in this Workshop.

The two co-organizer countries agreed to pursue these objectives by convening a group of experts both from within and outside the two Governments. The experts were selected among those with internationally or nationally recognized expertise and so as to achieve a balanced representation of existing viewpoints and diverse experiences. A list of all Workshop participants and their affiliations is attached here as an appendix. Because of the substantial commitments in time and effort required of them, the non-Government experts were offered monetary compensations.

The organizers agreed, further, on a Workshop format that was to dedicate 2 full days to pre-prepared presentations and followup discussions, one-half day to a plenary discussion, and the last full day to Steering Committee discussions (see attached Workshop Agenda). The Workshop Steering Committee, composed of four non-Government participants, guided the Workshop discussion so as to adhere to the Workshop objectives and, at the end, digested all information presented at the Workshop and reported it in terms of relevant conclusion statements and recommendations included here.

2.0 MAGNITUDE AND TRENDS OF OZONE PROBLEM

2.1 Ozone Problem in Europe

The general features of the ozone distribution throughout Europe have slowly emerged over the last 15 years since ground level measurements commenced. Elevated hourly ozone concentrations over 60 ppb have been observed at some time during almost every year at every site. The frequency of occurrences of higher hourly concentrations falls off so that 120 ppb is exceeded only during certain years and at certain sites. The extreme hourly ozone concentrations reported for each country cover the range 100-300 ppb. Meteorological conditions conducive to photochemical ozone episodes are those within high pressure systems during summer with clear skies and low windspeed. The vertical mixing is then inhibited and precursors and oxidants can accumulate. In urban areas averaged ozone concentrations are generally lower compared to adjacent rural (downwind) areas most likely due to chemical destruction of ozone by emitted NO. Quantitative identification of trends is complicated by the short observational record, year-to-year variability in the weather, changes in measurement method and calibration techniques and changes in emission patterns. Sub-micron particles can serve as an indicator of large-scale anthropogenic pollution as well as PAN. PAN is, in addition, an excellent indicator of high photochemical activity. Ozone and PAN show a similar behavior both in their seasonal cycle and diurnal variation[2].

In the Federal Republic of Germany, there were 156 ozone monitoring stations operating during 1987. Most of them are situated in urban areas. The measurements are based on chemiluminescence and UV absorption techniques. Ozone data up to 1983 have been published in a review report[3]. Table 2-1 shows ozone concentrations form 1976 to 1986 at some selected sites across the Federal Republic of Germany. These measurements indicate the average annual ozone concentration to increase with altitude and with distance from urban areas, presumably due to dry deposition at the ground and the influence of NO emission. Typical annual averages ranged between 20 and 80 $\mu g/m^3$ (10 and 40 ppb). The records also show both a seasonal and diurnal cycle. The seasonal cycle has a minimum in winter and a maximum in summer. In general, the annual amplitude decreases with altitude. Maximum ozone concentrations are highest at low altitudes close to certain industrialized and urban areas. They occur during episodes in summer, when high pressure systems over Central or Northern Europe are accompanied by easterly flow from the continent and high temperatures. Vertical ozone profiles taken by airplane under these conditions show that ozone concentrations in excess of those found in the middle troposphere are abundant in the mixing layer all over the warm part of such high pressure systems. The spatial extent of these elevated ozone concentrations is of the order of a million square kilometers. On this regional scale 200 $\mu g/m^3$ (0.10 ppm) appears to be the upper limit for ozone within the mixing layer as shown in Figure 2-1[3]. Higher concentrations are due to local sources. The highest ozone concentration ever observed near the surface in Germany is 664 $\mu g/m^3$ or 0.34 ppm (30 min. average) on June 23, 1976, in Mannheim (Upper Rhine Valley)[3]. Due to different meteorological conditions from year to year the frequencies of exceeding certain ozone concentration

Table 2-1. Recent O_3 concentrations measured at selected sites in the Federal Republic of Germany ($\mu g/m^3$)

Years:		1979	1980	1981	1982	1983	1984	1985	1986
Northern Part									
Westerland/Sylt	(1)	-	62	64	58	-	58	60	-
(seaside)	(2)	-	82	78	-	-	-	-	-
	(3)		150(b)	168(b)	126(b)	-	192(b)	166(b)	-
Hamburg	(1)	15	24	27	28	25	-	-	-
(urban)	(2)	21	34	40	35	35	-	-	-
	(3)	130(c)	136(c)	168(c)	160(c)	168(c)	-	-	-
Waldhof	(1)	-	60	-	54	84	50	50	-
(rural)	(2)	-	77	-	-	99	-	-	-
	(3)	-	244(b)	270(b)	230(b)	320(b)	182(b)	286(b)	-
Western Part									
Eggegebirge	(1)	-	-	-	-	-	42	51	57
(rural)	(2)	-	-	-	-	-	58	68	75
	(3)	-	-	-	-	-	200(a)	243(a)	233(a)
Cologne	(1)	20	21	-	31	24	22	21	21
(urban/center)	(2)	30	32	34	48	38	31	33	30
	(3)	210(a)	240(a)	382(a)	306(a)	304(a)	282(a)	214(a)	196(a)

Table 2-1 (Cont'd)

Cologne	(1)	23	23	-	37	33	19	22	22
(suburb)	(2)	32	36	50	52	51	26	34	32
	(3)	190(a)	240(a)	546(a)	326(a)	304(a)	242(a)	202(a)	178(a)
Eifel	(1)	-	-	-	-	-	51	54	63
(rural)	(2)	-	-	-	-	-	63	72	77
	(3)	-	-	-	-	-	217(a)	203(a)	251(a)
Southwestern Part									
Deuselbach	(1)	-	62	58	56	54	54	52	-
(rural)	(2)	-	88	72	78	67	-	-	-
	(3)	-	290(b)	194(b)	220(b)	184(b)	188(b)	196(b)	-
Mainz	(1)	56	32	32	35	27	33	27	33
(urban)	(2)	80	45	43	53	37	48	41	44
	(3)	410(a)	319(a)	217(a)	268(a)	187(a)	359(a)	228(a)	208(a)
Mannheim-Nord	(1)	27	24	28	-	36	34	30	29
(urban)	(2)	43	36	44	59	62	-	-	-
	(3)	198(d)	214(d)	257(d)	397(d)	294(d)	281(d)	200(d)	211(d)
		-	-	-	-	-	398(a)	210(a)	224(a)
Mannheim-Mitte	(1)	27	25	-	40	32	29	28	25
(urban)	(2)	46	38	-	57	-	-	-	-
	(3)	244(d)	193(d)	-	408(d)	187(d)	199(d)	254(d)	208(d)
		-	-	-	-	-	231(a)	336(a)	241(a)

Table 2-1 (Cont'd)

Ludwigshafen (urban)	(1)	34	28	27	34	37	29	27	25
	(2)	48	40	35	48	54	41	39	35
	(3)	289(a)	218(a)	197(a)	268(a)	278(a)	268(a)	177(a)	278(a)
Schauinsland (rural/1205m)	(1)	-	97	70	78	78	82	75	-
	(2)	-	113	-	94	95	-	-	-
	(3)		311(b)	157(b)	231(b)	221(b)	209(b)	176(b)	-
Southern Part									
Brotjacklriegel (rural/1016m)	(1)	-	57	71	74	74	58	60	-
	(2)	-	63	88	86	96	-	-	-
	(3)	-	143(b)	172(b)	184(b)	198(b)	181(b)	154(b)	-
Hohenpeißenberg (rural/1000m)	(1)	58	60	65	70	60	62	66	66
	(2)	74	73	78	86	73	79	82	78
	(3)	188(b)	166(b)	168(b)	240(b)	158(b)	260(b)	188(b)	164(b)

Notes: (1) annual mean, (2) summer mean (April-Sept.)
(3) max. values: (a) 0.5 hour average, (b) 1 hour average, (c) 3 hours average, measuring stations above 1000 m sea-level have been corrected for pressure

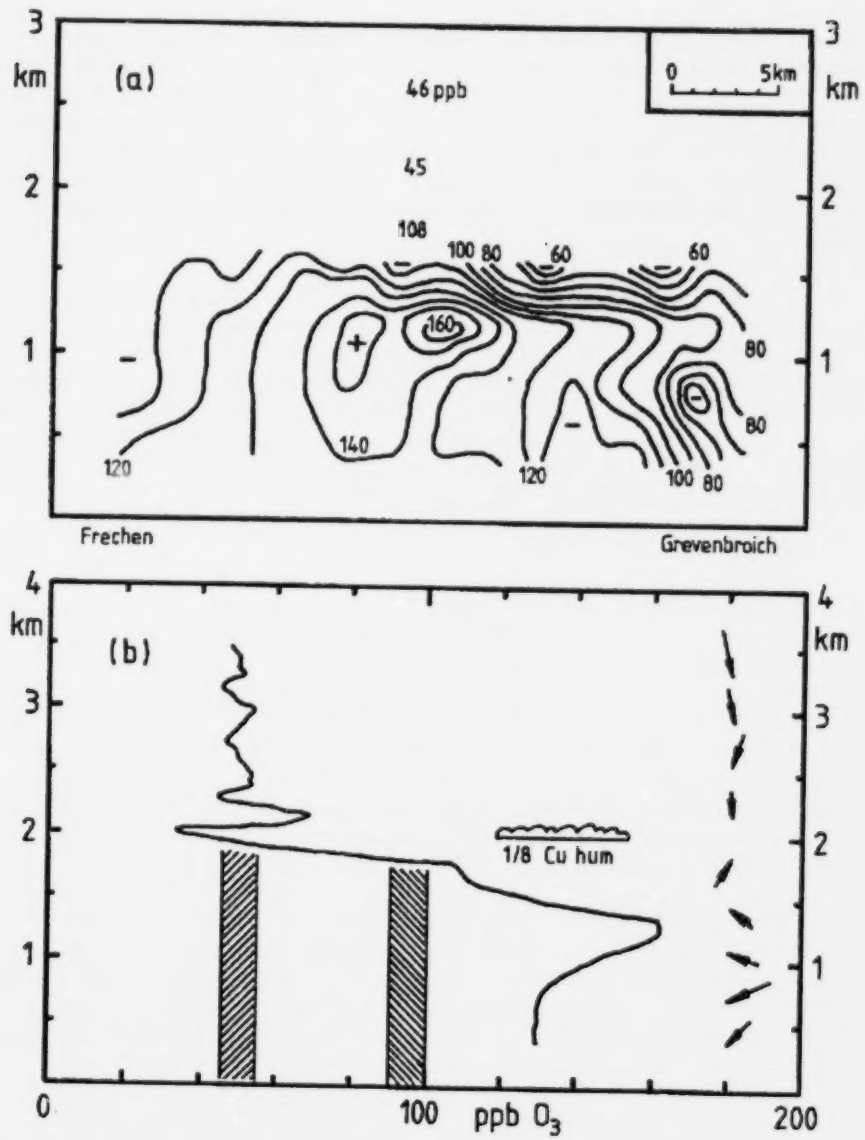


Figure 2-1. Airborne ozone measurements in the Cologne area on June 26, 1976:

(a): O_3 concentration cross-sections down-wind of Cologne between Frechen and Grevenbroich, 14^{00} - 14^{30} CET

(b): Vertical profile in the zone of max. O_3 concentration, left bar: concentration above the mixing layer; right bar: advective contribution within the mixing layer; wind vectors were taken from balloon soundings north of Cologne

levels vary considerably. Concentrations of 300 $\mu g/m^3$ (0.15 ppm) are exceeded more often close to precursor sources. At lower exceedance levels the frequency of episodes increases as one goes from urban to rural or mountain areas. At the same time the maximum concentrations themselves decrease. In the Cologne area measurements above an olefin plant (Figure 2-2)[3] showed that the stationary olefin plume is closely associated with elevated ozone concentrations probably due to a low $NMVOC/NO_x$ ratio in this area.

A detailed analysis of all available data indicates that the ozone burden increases going from the north to the south of Germany. Whether the upwards trend of ozone concentrations observed in the 1970's can be attributed to an increase of NO_x emissions during that time is not really established, but would offer a reasonable explanation. Insufficient data on VOC are available in order to evaluate the $NMVOC/NO_x$ ratio across Germany. Some data indicate that in densely populated areas the value of this ratio favors ozone control by NMVOC control.

2.2 Ozone Problem in the US

Ozone monitoring was initiated in the US in the early 1950's, in a network of stations in the Los Angeles Basin that measured ozone and other oxidants by the potassium iodide (KI) method. The network was expanded in the early 1960's to several major urban areas, and since 1971, when USEPA promulgated the first ozone air quality standard, it has adopted the ozone-ethylene chemiluminescence method for ozone measurement. Today every US urban area with a population greater than 200,000 is required to have at least two ozone monitoring sites. Of these, some 242 have been generating monitoring data in the last ten years that were sufficiently complete for use in ozone trend studies.

There are several ways in which the magnitude of the ozone problem can be expressed, for example: annual maximum (or second maximum) 1-hr ozone concentration, smog season (or annual) average daily maximum (or second maximum) concentration, and number of days or hours (per year) for which the ozone concentration exceeded the US ambient air quality standard of 0.12 ppm. In general, the most robust measures (e.g. annual average) suffer less from uncertainties due to spurious influences. However, they are also less useful, e.g. their inherent lower variability makes them difficult to relate to factors affecting ozone formation or to effects. The least robust measures of air quality (e.g. annual maximum) are preferable as measures of "most unfavorable situations" but they also suffer most from uncertainties. It should be stressed also that besides random errors, measurements of peak ozone concentration may suffer from a negative bias because of the limited density of the ozone monitoring stations. In judging the magnitude of an ozone problem, therefore, it is important that proper consideration be given to the ozone air quality index used and also to the relative abundance of the monitoring data used to determine the level of ozone air quality.

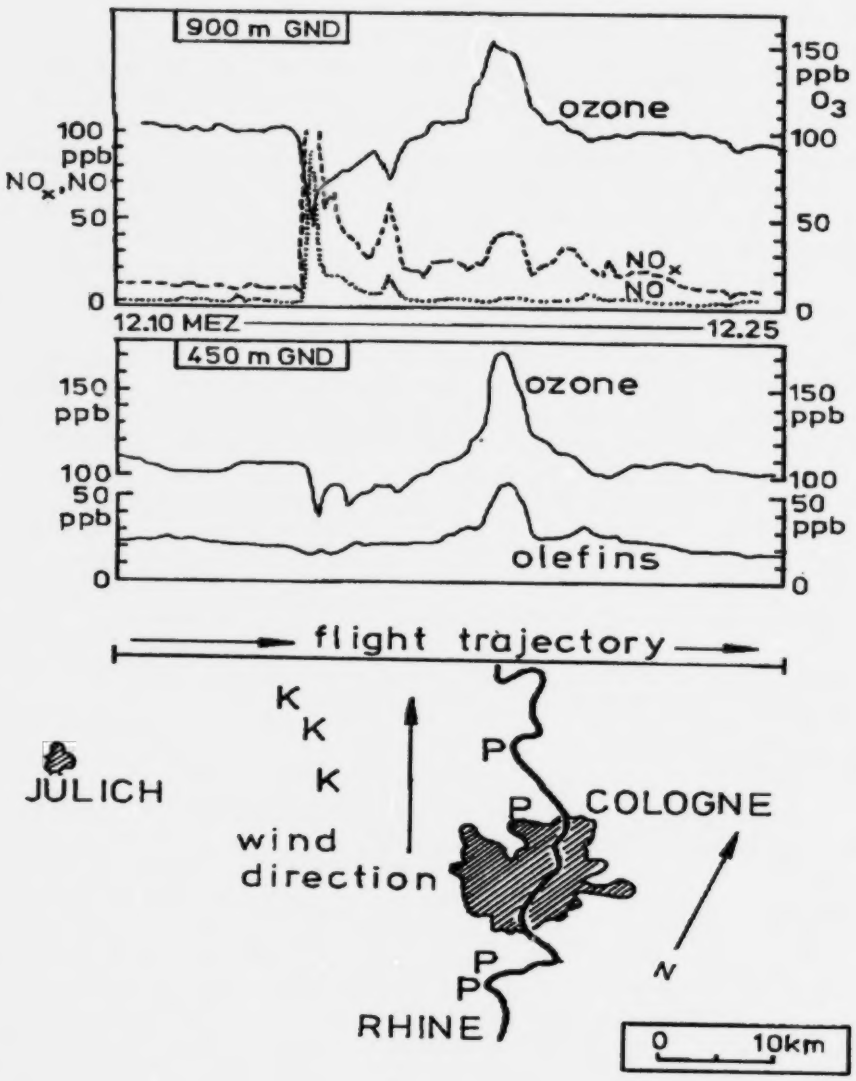


Figure 2-2. Concentration profiles of ozone, NO, NO_x, and olefins downwind of Cologne, 450 and 900 m above ground. The NO_x maxima and the corresponding ozone minima are attributed to the plumes of large lignite-burning power stations (K power station, P petrochemical plant)

The ozone air quality data given here for the US were taken from previously published reports[4] and were selected so as to provide two different measures of the ozone problem in the US: one in terms of peak ozone concentrations and one in terms of frequency of violations of the ozone air quality standard. Figure 2-3 shows levels of second maximum daily 1-hr concentrations in a variety of attainment (of ozone standard) and non-attainment urban areas in the US. Figure 2-4 shows exceedances of the ozone standard at the non-attainment urban areas. The two figures show that the most severe ozone problems in the US occur in urban areas within California, the Northeast States and the Gulf Coast area. The ozone standard was exceeded in some urban areas within California during the 1983-86 period up to 140 days and peak ozone concentrations observed in some urban areas of California in 1985 were as high as and even higher than 0.35 ppm. Figures 2-5 and 2-6 show ozone data averaged over 242 urban locations, depicting trends during the 1977-1986 period. The data reflect a significant decrease of ozone concentrations with time, but there are two apparent "anomalies": the strong deviation of the 1983 concentration from the pattern and the rather abrupt ozone decrease from 1977-78 to subsequent years. A detailed examination of ozone trends for individual urban areas showed the year 1983 to be consistently associated with higher ozone concentrations, suggesting that the 1983 "anomaly" can be attributed to meteorological conditions being more conducive to ozone formation than those in the adjacent years. The sharp ozone decrease from 1977-78 to the subsequent years has been found to be partly due to a change of the calibration method used for ozone measurement. After adjustment for this artifact, however, the data still showed a significant downward trend for the ozone concentration during the 1977-86 period.

2.3 Background Ozone

Ozone occurring in atmospheres not directly impacted by anthropogenic emissions is referred to as background ozone. Levels of such ozone are dependent upon: (1) the state of the stratospheric ozone reservoir and its exchange rate; (2) the chemical precursor content of the troposphere; (3) actinic photon fluxes; (4) the nature of the surface exposed; and (5) horizontal transport. These important, but not all inclusive parameters, would suggest that background ozone levels should show temporal/seasonal, latitudinal and altitudinal dependence as well as dependence with regard to a marine versus a continental environment. Some data relevant to this suggestion are given in Table 2-2. With the qualifying dependencies, ozone background concentrations range typically from 20 to 40 ppb in rural/remote regions. Figure 2-1 shows that in free troposphere (June 26, 1976, Cologne area) the ozone concentration is about 50 ppb. Figure 2-7 which presents the frequency distribution of the ozone concentration as 1-hour values averaged over the period 1977-81 at different sites in South Germany, indicates that 35 to 40 ppb seems to be a typical ozone concentration in the unperturbed troposphere.

The typical vertical distributions of ozone in the troposphere at remote sites are presented in Figure 2-8. Trends in background ozone levels reported at NOAA/GMCC baseline stations, Figure 2-9, indicate increases at sites in the Northern Hemisphere while sites in the Southern Hemisphere

Figure 2-3. Ozone concentrations in urban areas of the United States

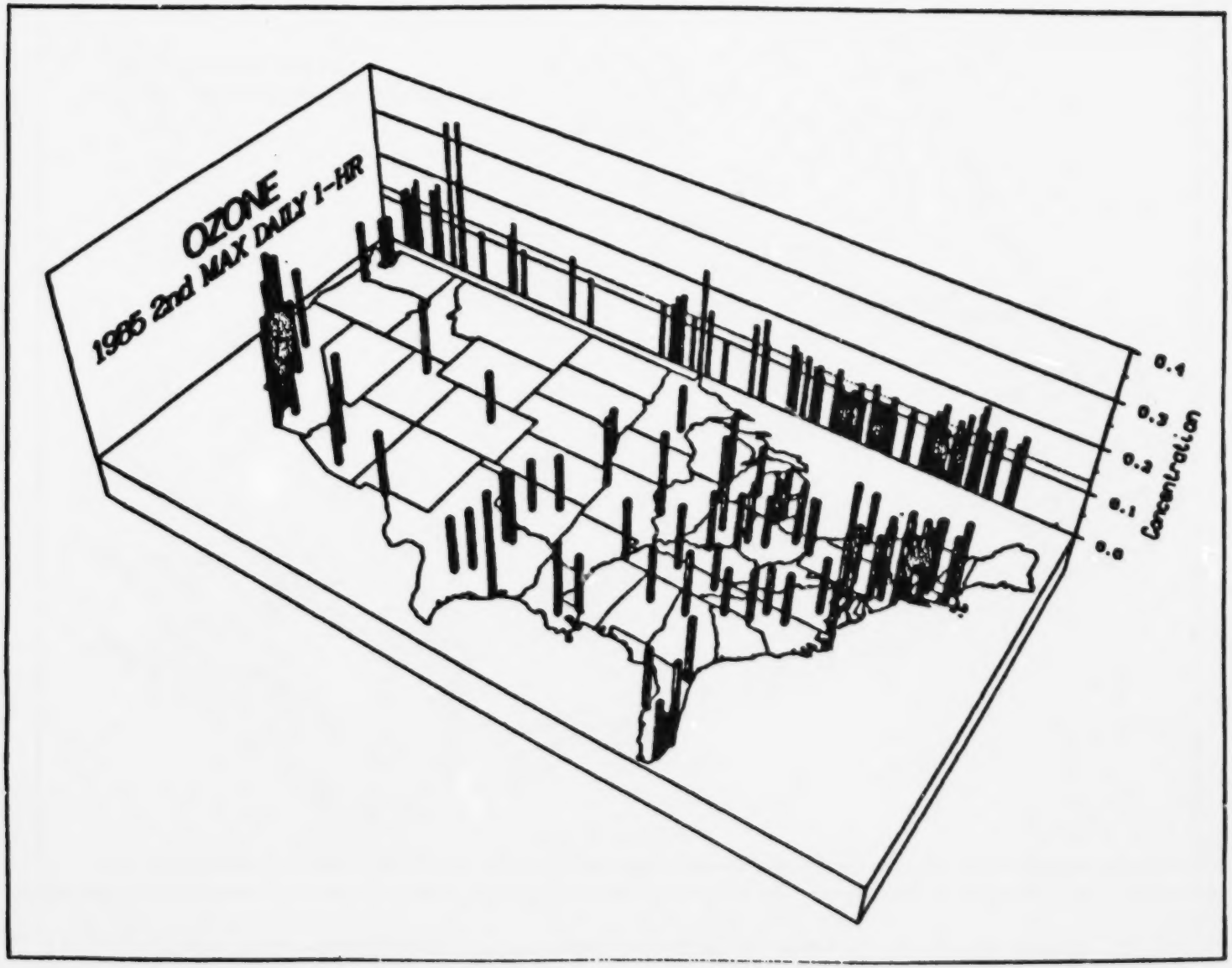
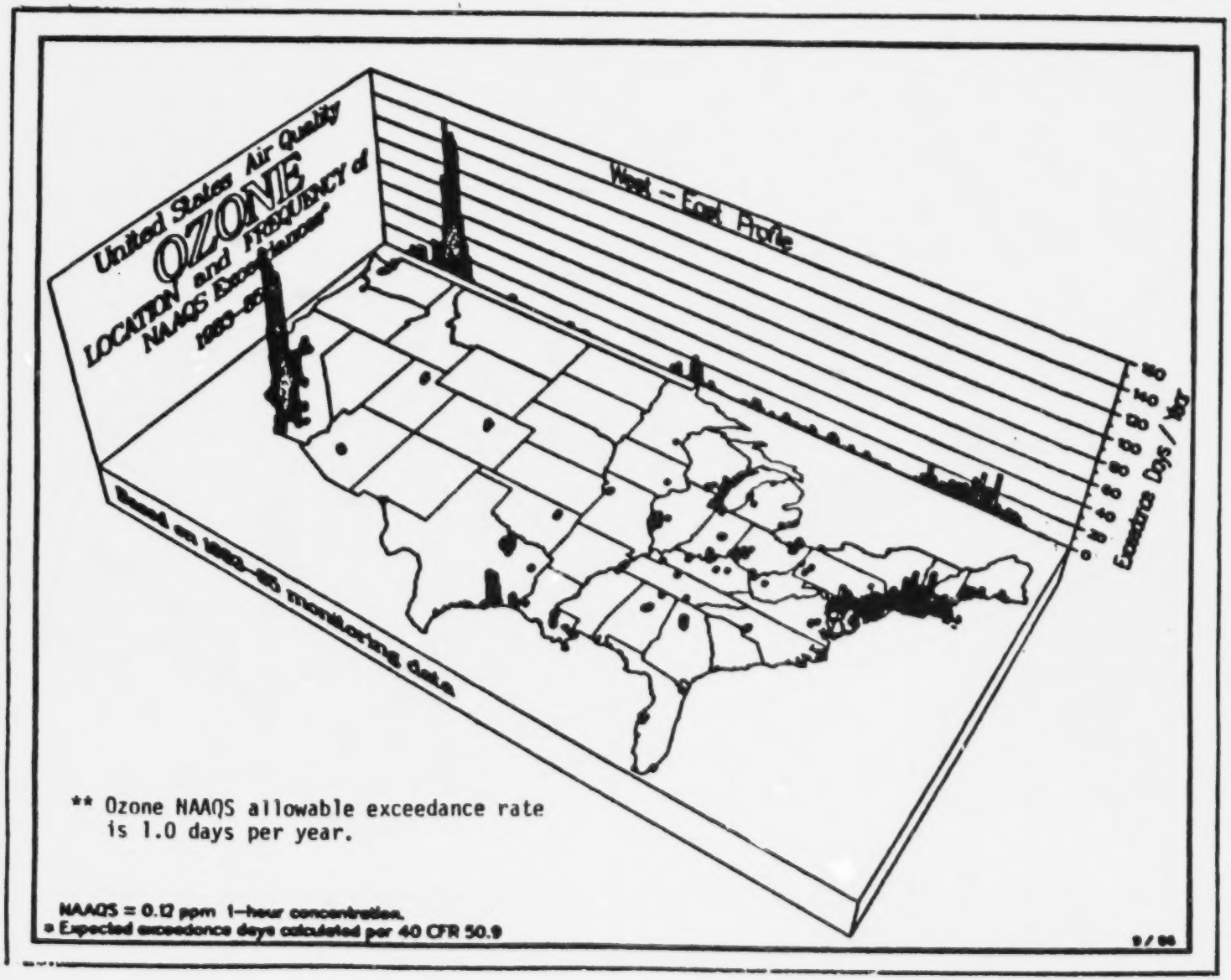


Figure 2-4. Exceedances of ozone standard in urban areas of the United States


United States Air Quality
OZONE
LOCATION and FREQUENCY of
NAAQS Exceedances*
1985-87
West - East Profile
Expected Days / Year
0 4 8 8 8 8 8 8
Based on 1985-87 monitoring data
** Ozone NAAQS allowable exceedance rate
is 1.0 days per year.
NAAQS = 0.12 ppm 1-hour concentration.
* Expected exceedance days calculated per 40 CFR 50.9
9/88

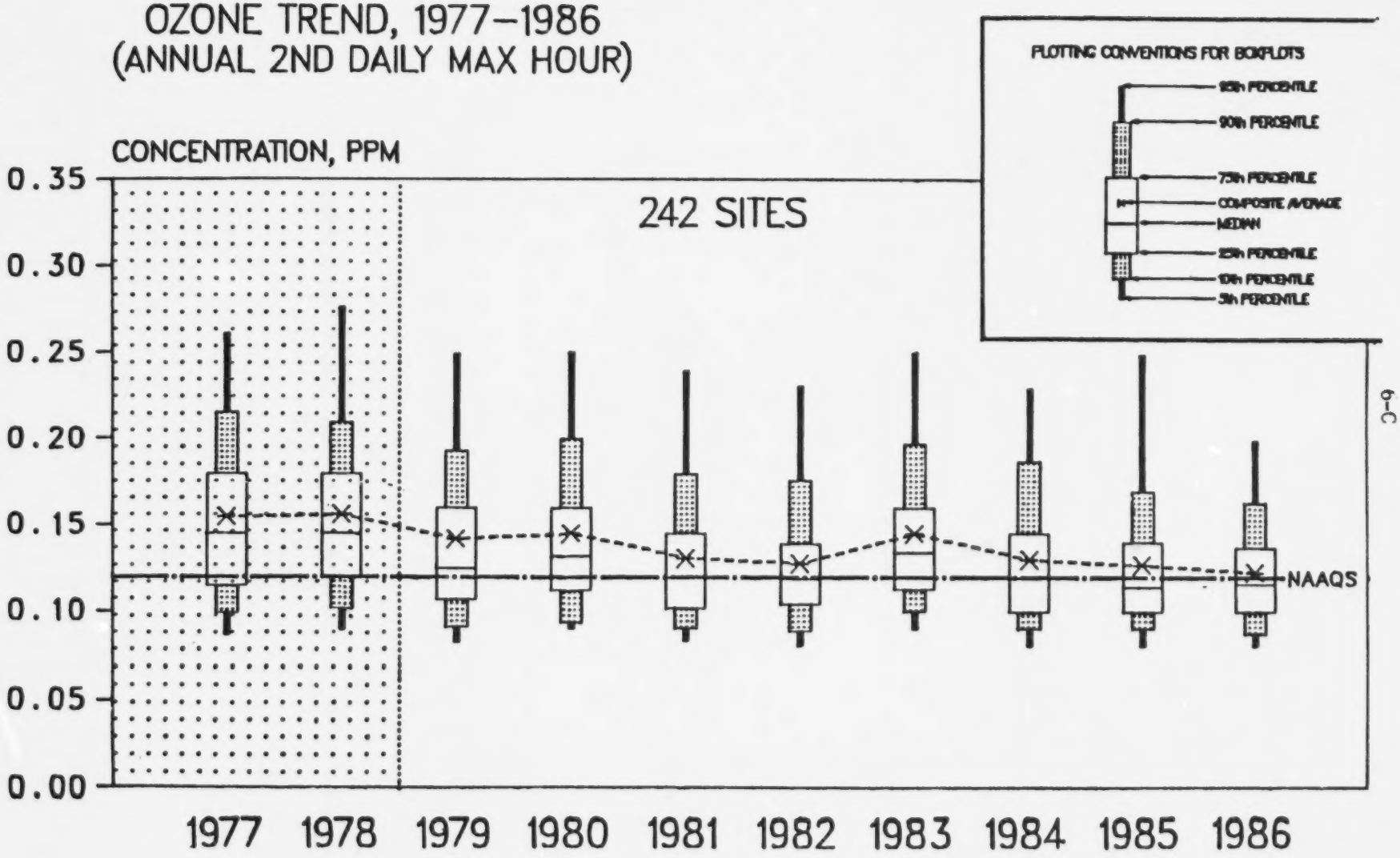


Figure 2-5. Boxplot presentation of U.S. ozone trends, 1977-86.

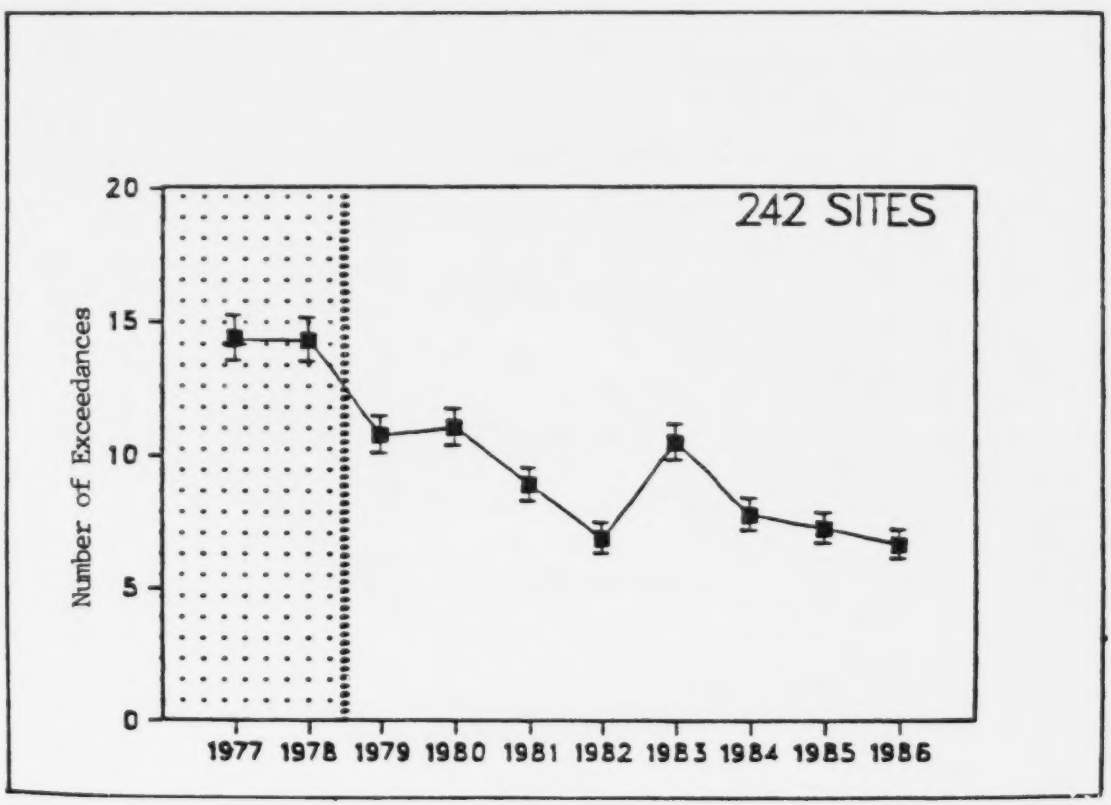


Figure 2-6. Trend in exceedances of U.S. ozone standard, 1977-86.

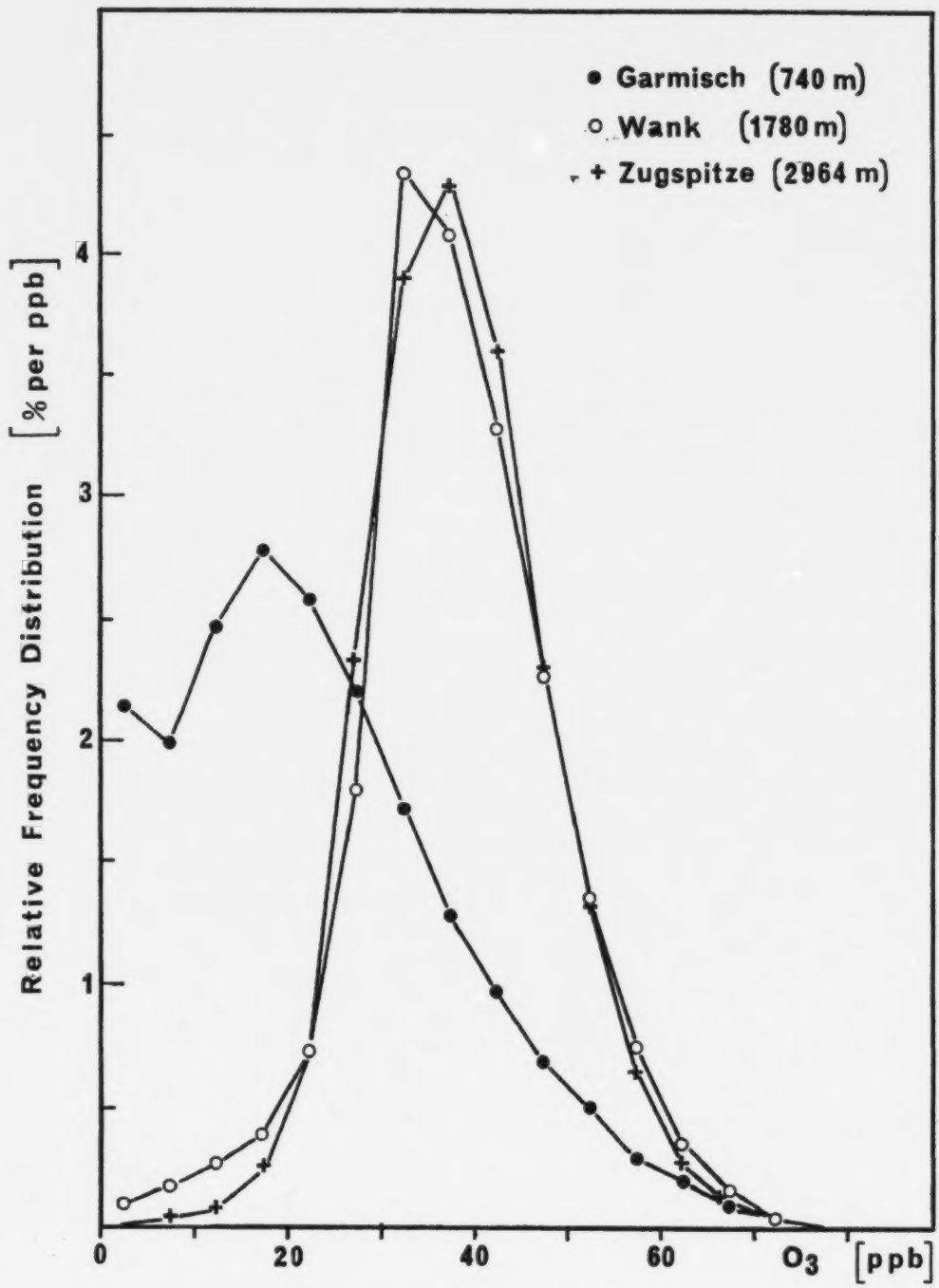


Figure 2-7. Frequenzy distribution of the ozone concentrations (1 h average) between 1977 - 1981 at the stations Garmisch (•), Wank (o), and Zugspitze (+), Federal Republic of Germany

Table 2-2

Typical Surface Ozone Background Concentrations (ppb)
at Remote Sites in 1986

Characteristic Environment	Hemisphere			
	NH		SH	
	Apr-Sep	Oct-Mar	Apr-Sep	Oct-Mar
Hilo, HI	20.5	20.5		
Samoa			18.3	17.5
Boulder, CO	39.1	29.3		
Whiteface Mt., NY	45.2	34.2		
Barrow, AK	19.4	26.3		
South Pole			18.5	13.9

Source: GMCC Summary Report 1986, No. 15, 1987; Whiteface Mountain Annual Summaries 1986.

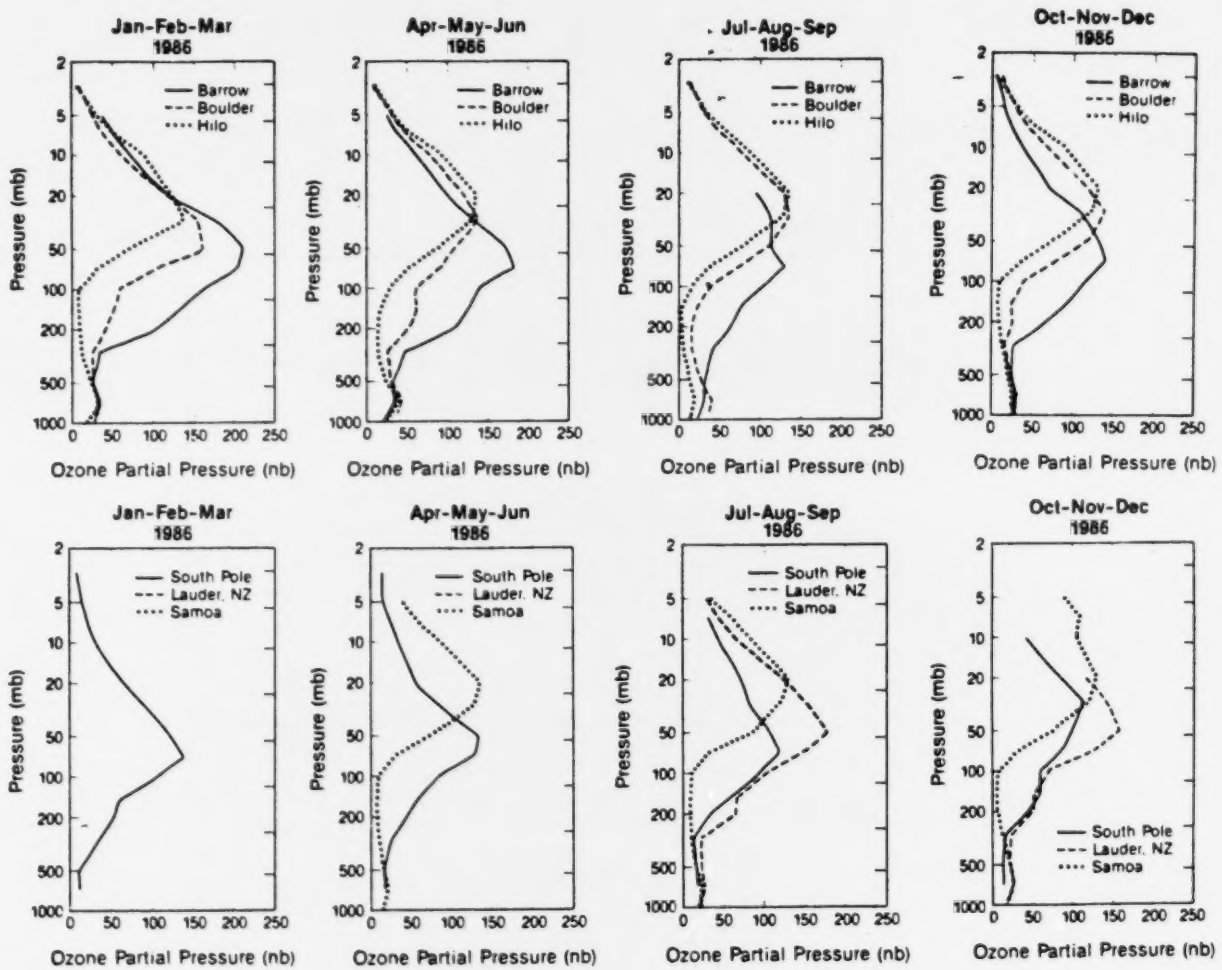


Figure 2-8. Mean seasonal ECC ozonesonde vertical distributions for the Northern Hemisphere (top) and the Southern Hemisphere (bottom). from the six-station GMCC sonde network.

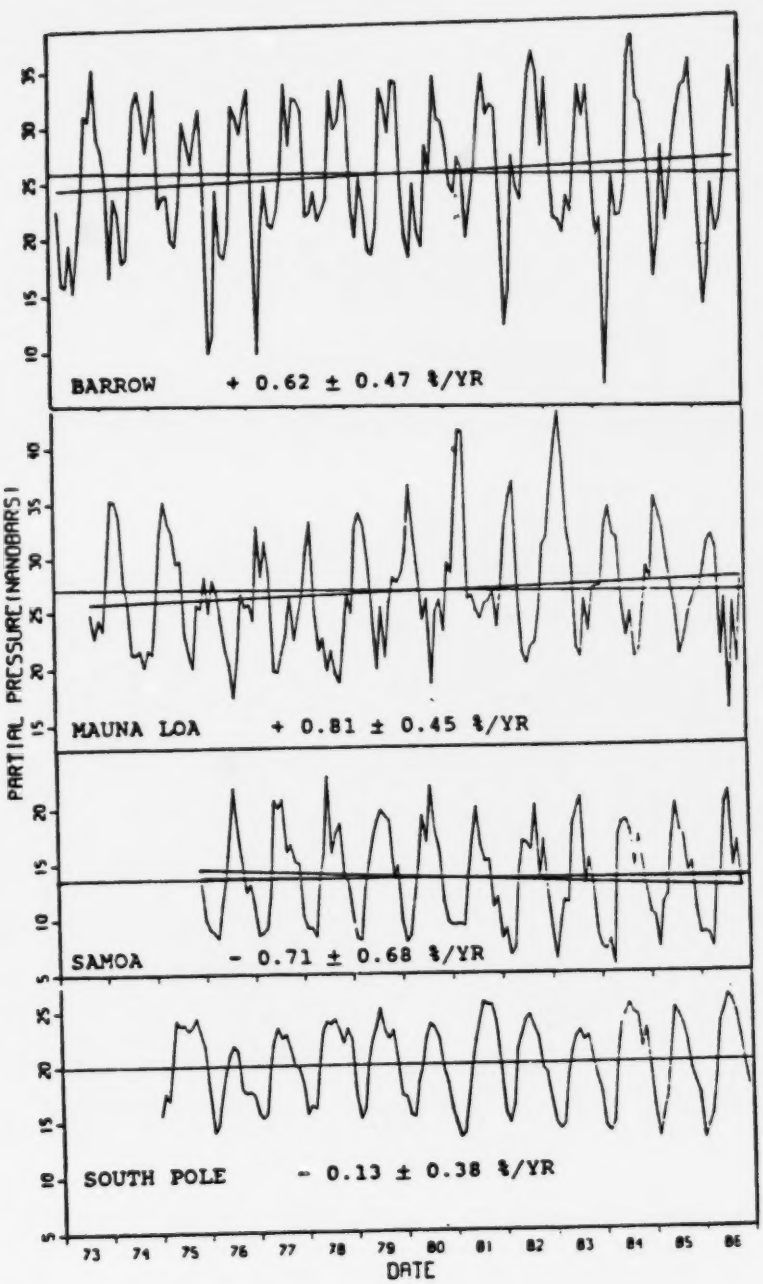

BARROW + 0.62 ± 0.47 %/YR
MAUNA LOA + 0.81 ± 0.45 %/YR
SAMOA - 0.71 ± 0.68 %/YR
SOUTH POLE - 0.13 ± 0.38 %/YR
PARTIAL PRESSURE (NANOBARS)
DATE
73 74 75 76 77 78 79 80 81 82 83 84 85 86

Figure 2-9. Monthly mean surface ozone values at the NOAA/GMCC baseline stations for 1973-1986. Also shown is the linear trend and 95% confidence interval in percent per year.

show the ozone concentrations to decrease with time. Interpretation of these trends, however, is somewhat speculative, given the various factors affecting ozone concentrations in the troposphere. Additional evidence of increasing ozone trends in continental environments include the observations at Arkona (GDR) and Hohenpeissenberg (FRG) and the historical account constructed for Montsouris, France (Figures 2-10 and 2-11). At Arkona, ozone increases between 1% and 3% or by 0.37 ppb per year, if a linear regression analysis is made. This station, which is continuously reporting since 1956, has the longest record of recent times. Somewhat shorter, starting in 1971, is the Hohenpeissenberg record where an annual increase of 0.41 ppb is observed. Although, as seen in Figure 2-10, the two German stations show somewhat different absolute levels of ozone over the time that they can be compared, the trends in units of ppb per year are quite comparable.

Crutzen[5] and Kley and Volz[6] have arrived at the conclusion that the current trend of ozone in western Europe began about 1940. Compared to the Montsouris series (Figure 2-11), which was obtained from 1876 to 1905 near Paris, background ozone concentrations in Europe have increased since then considerably[7,8]. An upward trend of the ozone concentration has been observed in the free troposphere and the upper part of the boundary layer between 1967 and 1982 over South Germany at Hohenpeissenberg (Figure 2-12)[9]. Measurements from East Germany[10] support the ozone increase near the surface between the mid-1950's and 1984; however, they do not show a significant ozone increase within the free troposphere at 5.5 Km altitude in the monitoring period 1975-84. Model calculations[11] suggest that this ozone increase can be attributed to the increase of NO_x emissions.

An increase of background ozone might be occurring in most parts of the Northern Hemisphere. Monitoring data suggest that increases are occurring, for example, at Barrow, Alaska and Mauna Loa, Hawaii (see Figure 2-9). The latter station, situated at an altitude of 3000 m, samples air that is characteristic of the free troposphere. Therefore, two stations, apart by nearly 180° of longitude experience a similar phenomenon.

It is extremely important for the assessment of the role of ozone transport to know the latitudinal dependence of this molecule between the North American and European Continents. No trends of ozone have been reported over the Atlantic Ocean. The meridional cross section of surface ozone is reproduced in Figure 2-13. It was obtained mostly along the 30° meridian. The simultaneously measured vertical ozone profiles are also reported in Figure 2-13. They show that, north of 20° northern latitude, there was hardly any vertical gradient of ozone in the lower troposphere so that the surface values are representative for the lower troposphere. A comparison of Figure 2-13 with the values measured at Hawaii (20°N) and Boulder (40°N), respectively (see Table 2-2), shows good agreement at corresponding latitudes. Figure 2-13 represents the best information on the large scale features of surface ozone between the American and European continent. It is not possible, at present, to specify the surplus of background ozone in the Northern over the Southern Hemisphere in terms of anthropogenic causes versus natural ones, i.e. a higher flux of ozone from

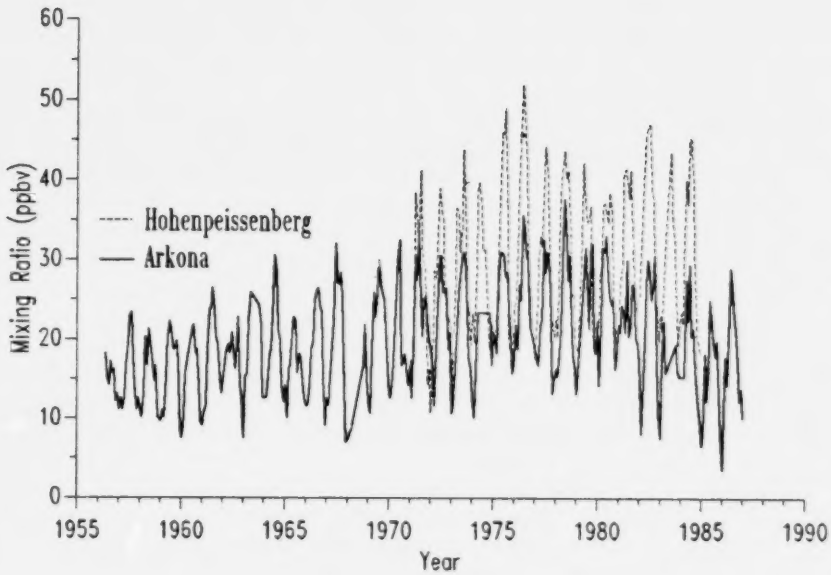


Figure 2-10. Ozone Trends in Hohenpeissenberg (FRG) and Arkona (GDR)

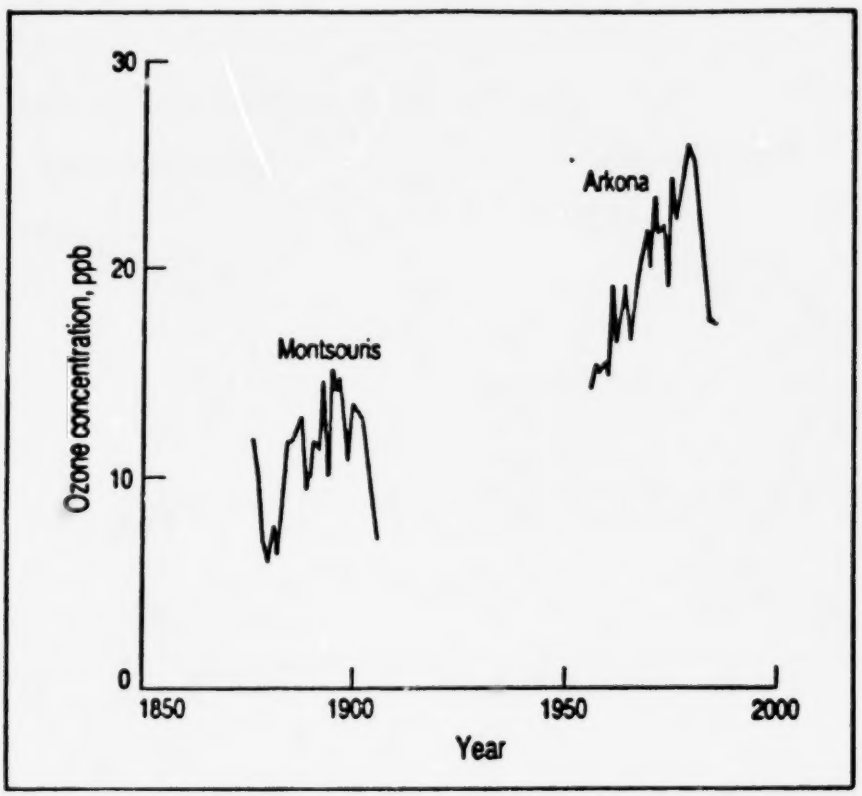


Figure 2-11. Near surface ozone concentrations (annual means) measured at Montsouris, France 1876-1905 and Arkona, German Democratic Republic 1956-1984.

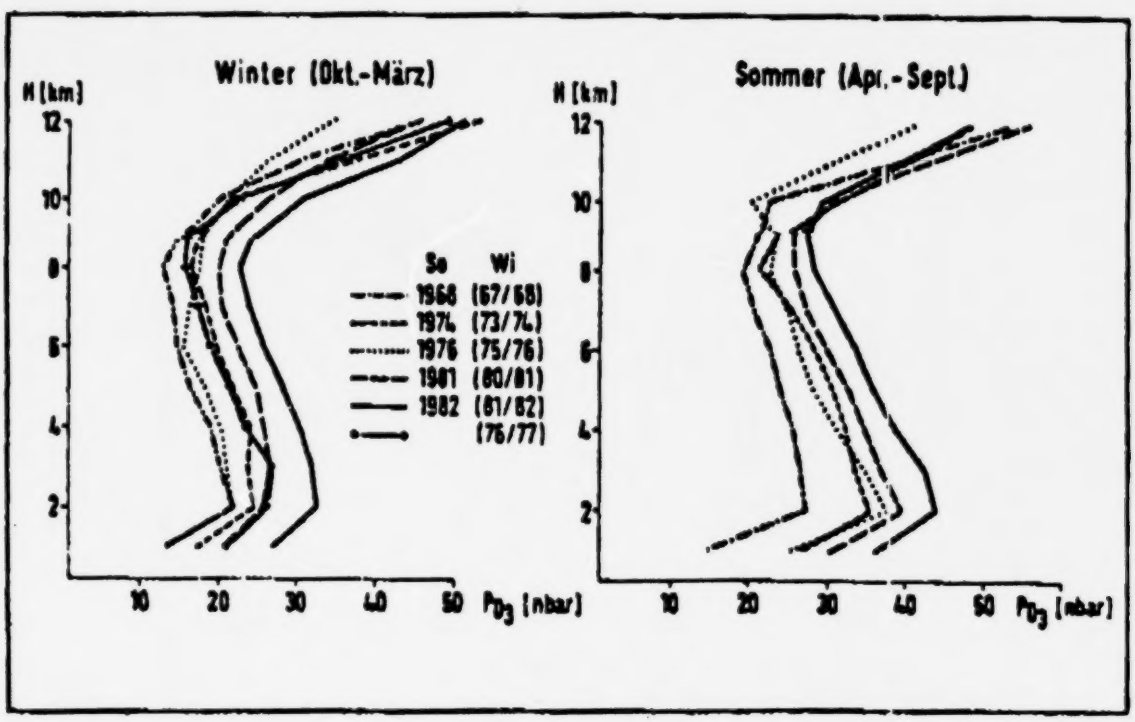


Figure 2-12. Vertical ozone distribution over Hehenpeissenberg, FRG[9]

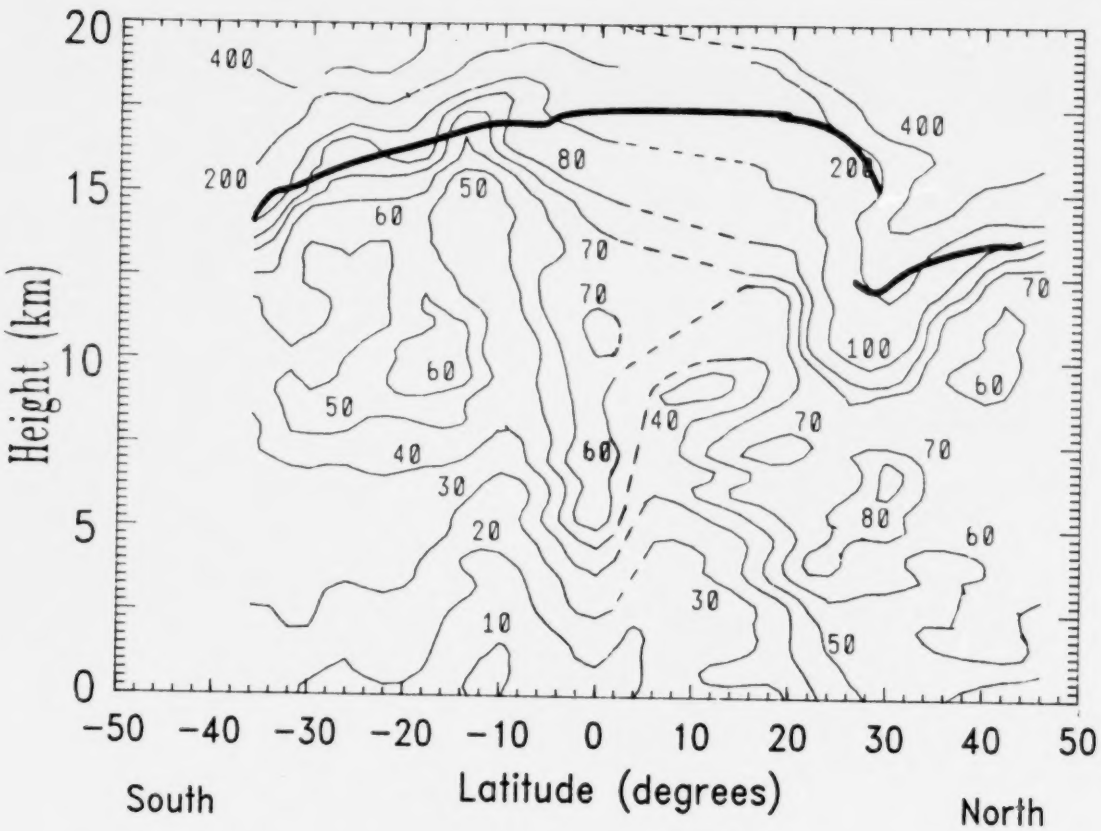


Figure 2-13. Meridional cross section of ozone (ppb) along 30° longitude during spring 1987[12]. The stratopause is indicated by the thick line.

the stratosphere. This is a major question that needs to be experimentally addressed.

Unlike Europe, background ozone concentration data for the US are scarce because few non-urban areas are routinely monitored for ozone concentrations. Some data are available, however, from special purpose networks, e.g. the National Air Pollution Background Network. Maximum 1-hr concentrations observed in rural sites approach and even exceed the air quality standard of 0.12 ppm. Generally, sites within 100 km of major urban areas exhibit the highest maximum concentrations, suggesting that such sites are influenced by urban ozone plumes. Average concentrations measured in a small network of rural sites not likely to be impacted by large urban plumes during summer range from 30 to 50 ppb, while averages of daily maximum concentrations are between 45 ppb and 65 ppb[13].

3.0 EMISSIONS

3.1 Emissions in Europe

3.1.1 Anthropogenic Emissions in Europe

The OECD together with the Commission of the European Communities has compiled an emission inventory for SO_2, NO_x and VOC (excluding methane, except in the mobile source sector) for 1980. These data are for all 17 Western European countries. They are broken down into approximately 80 source categories (i.e. economic sectors) and subcategories (i.e. emission generating processes), and are also geographically allocated to the 50 X 50 Km EMEP subgrid. Currently, the OECD inventory is being reviewed by all member countries for national approval. The inventory will subsequently be published. For modeling work and other scientific research, the data can be made available upon request from OECD. Tables 3-1 to 3-3 show data on national emission totals for all 17 Western European Countries for SO_2, NO_x and VOC, respectively (data have not been approved officially by the countries yet). Tables 3-1 to 3-3 depict the geographical distribution of emissions in Western Europe. For more detail the reader is referred to Lübkert and de Tilly[14] and for NO_x, in particular, to Lübkert[15].

3.1.2 Biogenic VOC Emissions in Europe

The role of natural biogenic hydrocarbon emissions in Europe is uncertain but is unlikely to be large based on current understanding of the emissions from various tree types, forest areas and the chemistry of the hydrocarbons themselves. Emissions of isoprene from deciduous trees contribute directly to ozone formation in the same way as man-made hydrocarbons. Total European (excluding USSR) isoprene emissions amount to about 7 million tons per year compared with 10 million tons VOC per year from man-made sources. In the highly industrialized regions of Europe (Belgium, The Netherlands, Denmark, Federal Republic of Germany, German Democratic Republic and United Kingdom) the natural and man-made emissions differ by a factor of 10, being 7.0 and 0.7 million tons per year, respectively. Emissions of terpenes from coniferous trees contribute directly to ozone removal processes in the same way as dry deposition removal. Reaction between terpenes and ozone increases ozone destruction over forested regions but it is difficult to quantify the magnitude of this increase. Under the assumption that the terpenes always cause destruction over forested regions, the ozone removal rate by terpenes within Europe (excluding USSR) would amount to about 33 million tons per year which is about one-fifth to one-tenth of the dry deposition removal.

3.1.3 Emission Uncertainties in Europe

The OECD inventory was compiled based on European emission tests and should thus be representative of Europe. Further, according to unpublished information from Drs. Derwent and Stern, use of the inventory in long range transport models for secondary pollutants has given good agreement between model predictions and observations. Finally, repeated checks of internal consistency and against other data sets (developed e.g. by independent

Table 3-1. Total SO_2 Emissions by Country and Major Source Sector for 1980 (KT SO_2)

COUNTRY	MOBILE SOURCES	POWER PLANTS	NON-INDUSTRIAL COMBUSTION	TOTAL INDUSTRY	INDUSTRIAL COMBUSTION	INDUSTRIAL PROCESSES	MISCELLANEOUS	TOTAL BY COUNTRY
AUSTRIA	14.00	91.00	65.00	180.00	150.00	30.00	0.00	354.00
BELGIUM	22.00	395.10	108.90	197.30	158.70	38.60	0.90	727.20
DENMARK	15.35	221.54	156.46	90.20	90.20	0.00	3.47	461.01
FINLAND	17.00	85.00	102.00	380.00	136.00	244.00	0.00	584.00
FRANCE	146.02	1056.20	402.10	1947.00	1599.00	348.00	5.10	3556.42
GERMANY	107.46	1400.17	422.49	1262.45	1011.08	251.38	0.00	3192.57
GREECE	46.37	334.95	30.74	159.82	159.82	0.00	10.10	581.98
IRELAND	5.34	101.90	34.90	80.80	78.60	2.20	0.00	222.94
ITALY	171.36	1560.00	475.00	1377.00	977.00	400.00	23.84	3607.20
LUXEMBOURG	2.50	0.00	5.03	21.72	13.12	7.60	0.00	21.25
NETHERLANDS	36.70	195.30	13.50	206.30	145.80	62.50	7.70	461.50
NORWAY	15.08	0.00	14.60	108.20	47.10	61.10	0.55	138.43
PORTUGAL	10.72	91.60	4.15	162.26	87.45	75.81	0.00	269.73
SPAIN	100.90	1768.40	55.40	622.43	622.43	0.00	60.18	2607.31
SWEDEN	17.50	40.50	139.00	285.00	158.00	127.00	0.00	482.00
SWITZERLAND	8.62	2.40	31.50	89.00	89.00	0.00	0.00	131.53
UNITED KINGDOM	111.80	2866.00	263.00	1321.00	1321.00	0.00	172.00	4735.80
WESTERN EUROPE	850.73	10199.06	2317.76	8492.48	6844.30	1648.18	283.84	22143.87

Table 3-2. Total NO_x Emissions by Country and Major Source Sector for 1980 (KT NO_2)

COUNTRY	MOBILE SOURCES	POWER PLANTS	NON-INDUSTRIAL COMBUSTION	TOTAL INDUSTRY	INDUSTRIAL COMBUSTION	INDUSTRIAL PROCESSES	MISCELLANEOUS	TOTAL BY COUNTRY
AUSTRIA	146.00	20.00	10.00	40.00	30.00	10.00	0.00	216.00
BELGIUM	170.08	61.22	67.15	69.29	56.29	13.00	2.90	370.64
DENMARK	102.61	121.13	22.37	17.03	16.02	1.01	6.64	269.78
FINLAND	151.60	75.70	26.60	20.47	11.23	9.24	5.20	283.57
FRANCE	1167.66	280.00	213.00	396.30	334.40	61.90	705.00	2761.96
GERMANY	1594.90	608.01	182.30	580.06	383.16	196.90	0.00	2967.27
GREECE	135.56	21.30	8.27	34.35	28.74	5.61	34.11	230.59
IRELAND	32.75	26.70	4.40	10.00	7.60	2.40	0.00	74.85
ITALY	992.70	287.00	79.30	240.40	190.40	50.00	0.00	1599.40
LUXEMBOURG	12.12	0.00	2.07	12.58	8.98	3.60	0.05	26.82
NETHERLANDS	321.80	80.30	34.30	86.90	65.00	21.90	12.40	535.70
NORWAY	156.80	0.00	4.70	24.00	13.40	10.60	0.13	185.63
PORTUGAL	106.26	19.72	0.14	39.67	13.11	26.56	0.00	165.78
SPAIN	446.50	190.00	15.10	320.00	163.00	157.00	0.00	971.60
SWEDEN	201.00	10.00	48.00	69.50	35.80	33.70	0.00	328.50
SWITZERLAND	138.00	0.00	8.60	49.40	32.11	17.29	0.00	196.00
UNITED KINGDOM	703.00	851.00	65.00	258.00	228.00	30.00	47.00	1924.00
WESTERN EUROPE	6586.33	2657.08	788.30	2267.95	1617.25	650.71	813.43	13108.10

Table 3-3. Total VOC Emissions by Country and Major Source Sector for 1980 (KT VOC as measured)

COUNTRY	MOBILE SOURCES	STATIONARY COMBUSTION	INDUSTRIAL PROCESSES	STORAGE AND HANDLING	ORGANIC SOLVENT EVAPORATION	MISCELLANEOUS	TOTAL MAN-MADE
AUSTRIA	184.00	17.40	0.00	0.00	130.00	0.00	331.40
BELGIUM	117.07	13.82	35.9[illegible]	[illegible].88	128.00	4.87	312.70
DENMARK	88.33	3.5[illegible]	12.97	6.82	[illegible].38	[illegible].80	172.66
FINLAND	81.90	3.80	7.20	4.60	43.80	[illegible].00	161.30
FRANCE	1132.60	44.60	94.60	116.30	464.35	118.[illegible]	1972.45
GERMANY	1080.37	122.28	195.63	115.90	915.00	40.[illegible]	3470.88
GREECE	34.88	2.50	16.40	5.20	72.30	12.[illegible]	161.48
IRELAND	28.14	13.20	1.20	0.00	34.10	[illegible].00	76.64
ITALY	638.00	58.07	87.55	51.00	639.95	91.30	1565.87
LUXEMBOURG	4.61	0.72	0.33	1.20	3.50	0.[illegible]	10.91
NETHERLANDS	227.60	23.40	51.30	39.00	140.30	11.00	512.60
NORWAY	54.63	20.41	5.42	6.30	50.90	[illegible].91	138.67
PORTUGAL	54.10	0.70	3.52	3.00	75.00	22.88	159.20
SPAIN	362.00	11.07	30.75	24.10	329.00	34.50	791.42
SWEDEN	253.68	44.24	23.08	9.26	89.13	3.15	422.55
SWITZERLAND	92.00	46.66	67.58	19.37	84.85	0.00	310.40
UNITED KINGDOM	603.04	101.00	153.00	96.0[illegible]	630.00	92.00	1675.04
WESTERN EUROPE	4976.95	529.43	786.49	510.87	3920.87	439.56	11166.17

COUNTRY	NATURAL SOURCES	TOTAL
AUSTRIA	140.00	391.40
BELGIUM	35.00	347.70
DENMARK	46.77	219.43
FINLAND	522.00	683.30
FRANCE	998.30	2970.75
GERMANY	220.00	2690.88
GREECE	130.00	291.48
IRELAND	17.00	93.64
ITALY	550.00	2115.87
LUXEMBOURG	0.55	11.46
NETHERLANDS	14.00	526.60
NORWAY	180.00	318.67
PORTUGAL	266.00	425.20
SPAIN	1400.00	2191.42
SWEDEN	750.00	1172.55
SWITZERLAND	45.00	355.40
UNITED KINGDOM	71.00	1746.04
WESTERN EUROPE	5385.62	16551.79

research groups or within other international bodies) established the OECD/CEC inventory as the most complete and accurate one currently available for Western Europe. Nevertheless, concrete estimates of overall reliability and completeness are still lacking. For some individual source sectors uncertainty calculations have been carried out. For vehicular NO_x emissions, for example, Eggleston and McInnes[16] calculated an uncertainty of 40% which compared well with uncertainties measured in UK of 15% for SO_2, 45% for NO_x and 80% for VOC[17].

3.2 Emissions in the US

3.2.1 Anthropogenic Emissions in the US

Emission inventories used in the modeling of ozone concentrations must include the major precursor species, NO_x, hydrocarbons and CO. In the US major efforts have gone into producing nationwide emission inventories for the base years of 1980 and most recently, 1985. The inventory is constructed by assimilating annual emissions from major point sources provided by the individual states with estimates of area source emissions generally made by the USEPA using surrogate activity-level indicators for the emissions, such as statistics on VMT (vehicle miles traveled), population, housing, employment, etc. The level at which the area source emissions are estimated are annual totals by county within each state. The emissions must then be "disaggregated" to produce hourly gridded emissions for use by the air quality models. Spatial, temporal and species allocation factors must be applied to the annual point and area source emissions to accomplish the disaggregation. Considerable uncertainty is introduced into the emissions estimates by the disaggregation process (see later discussion of uncertainties).

The inventories are constructed such that total mass emissions are estimated for certain "classes" of emissions. For example, exhaust emissions from light-duty vehicles (most automobiles) might be one class, architectural surface coatings would be another, domestic solvents another, etc. Classes exist for every major industrial, commercial and residential point or area source emissions class. This is the Source Classification Code (SCC) system, an important building block in the emission inventory process. A profile of individual compounds with their associated weight percentages exists for each SCC code. In the disaggregation process the individual organic species are "lumped" together into similarly-reacting groups of compounds, such as olefins, paraffins, etc., in order to minimize the total number of species carried in the final gridded inventory. The particular groupings of organics are somewhat dependent on the chemical kinetic reaction scheme used by the air quality model.

Table 3-4.

1980 Continental US Emissions (NAPAP-Version 4.0) by Source Category (1,000,000 tons/year)

	SO_x	NO_x	VOC
Electric Utilities	17.3	8.1	0.1
Industrial Combustion	3.7	4.5	1.0
Residential/Commerical Combustion	0.9	0.7	0.1
Non-ferrous Smelters	1.2	-	-
Other Industrial Processes	3.0	1.0	4.5
Transportation	0.9	9.1	8.0
Miscellaneous	0.1	0.3	9.6
Total	27.1	23.7	23.3

Tables 3-4 and 3-5 present a summary of total anthropogenic emissions from the continental US and Canada from the NAPAP-Version 4.0 and 5.0 (final) emissions inventory for 1980.

3.2.2 Biogenic VOC Emissions in the US

Biogenic emissions of organic species have been estimated for the US in several recent studies. Regional modeling tests show that these compounds contribute to the total reactivity of the lower troposphere when sufficient NO_x is present. Emission factors for isoprene and monoterpenes have been estimated for many tree, crop and grass species in the US. The total mass of individual species have been estimated from land-use inventories satellite imagery. Although estimates of biogenic emissions are still in crude stages, the total mass of biogenic organics (29,000 tons/day) is of the same order of magnitude as the anthropogenic organics in the Northeast US where there are large contributions from the anthropogenic side. In the Northeast US, the total biogenic hydrocarbon is estimated to be 41% monoterpene, 18% isoprene, and 42% unidentified organics.

3.2.3 Emissions Uncertainties in the US

Estimates of uncertainty in the 1980 US inventory have been made subjectively by a panel of experts in the development of inventories. Table 3-6 shows these estimates for some of the principal component steps in the inventory development process for both anthropogenic and biogenic emissions. The uncertainties in VOC are generally greater than those in either NO_x or CO, and the species and temporal allocation processes introduce the greatest components of uncertainty in the emissions disaggregation. For the biogenics (Table 3-7), the temperature-dependence of the monoterpene emissions is a very uncertain factor. The estimated composite error Table 3-8) in the hourly gridded emissions varies from 109% for the biogenic VOCs to 33% for NO_x.

Table 3-5. 1980 NAPAP Emissions Inventory Version 5.0 - Area and Point Sources

Country	THOUSAND TONS/YEAR										
	SO2	SO4	NOX	PB	CO	HCL	HF	NH3	TSP	VOC	THC
Canada	5,109	188	2,054	NR	18,036	NR	NR	210	31,574	2,994	5,138
Contig. U.S.	26,954	976	22,352	32	99,309	527	115	839	42,617	23,165	24,977
Total	32,063	1,164	24,406	32	117,345	527	115	1,048	74,192	26,158	30,115

NR => Not Reported

Note: Numbers may not sum due to rounding.

Table 3.6

UNCERTAINTY ESTIMATES
1980 NAPAP Anthropogenic Emissions

Source of Uncertainty	Percent Error		
	VOC	NO_x	CO
Stack Test	25	25	25
Material Balance	50	25	25
Mobile	50	30	30
Seasonal Allocation	10	10	10
Daily Allocation	25	25	25
Hourly Allocation	75	50	75
Species Allocation	100	25	–
Spatial Allocation	25	25	25

Table 3.7

UNCERTAINTY ESTIMATES
1980 EPA Biogenic VOC Emissions

Source of Uncertainty	Percent Error
Emission Rate	91
Biomass Density	41
Allometric Biomass	30
Land Use Distribution	25
Temperature Adjustment	330
Spatial Allocation	25
Tree Type	19
Tree Size	3
Light/Temp. Correction	35

Table 3.8

UNCERTAINTY ESTIMATES
(Composite From All Sources of Uncertainty)

1980 ROM Grid-level Hourly Emissions

	Percent Error	
	(Point & Area)	(Area Only)
Speciated VOC (Anthropogenic)	64	74
Speciated VOC (Biogenic)	–	109
Speciated NO_x	32	33
CO	49	54

It is generally accepted that the anthropogenic VOC inventory has been underestimated. Indications of this come from a number of areas, including the disparities in the VOC/NO_x ratios in the emission inventories and 6-9 am ambient data (see next section), and the exclusion of some known VOC-emitting source types, including hazardous waste treatment facilities. The 1985 US inventory effort has made great strides in correcting many of the known deficiencies in the process of building an inventory. Among the improvements are the development of methodologies for missing source types, temperature-dependence of evaporative emissions from mobile sources, updating and improvement of temporal and speciation allocation factors, formalized and rigorous quality assurance procedures, and a high level of coordination with state and local pollution agencies involved with assimilating data for the inventories.

3.2.4 Ambient VOC/NO_x and VOC Composition in US

In 1984 the USEPA started an urban VOC data collection program that continued through 1988. In this program, local agencies collected 6-9 am integrated ambient air samples using SUMMA polished stainless steel canisters. These were shipped overnight to an EPA laboratory where they were analyzed by three different groups. In addition to using the cryogenic preconcentration direct flame ionization detection method (PDFID)[18], a large number of the canisters (ca. 900) were selected for detail speciation using gas chromatography[19,20]. The program involved extensive quality assurance procedures and the results demonstrate excellent precision and accuracy: on repeat analysis of 155 samples the precision for total non-methane organic compound concentrations (NMOC) was 0.49% and on fully duplicate samples (i.e. two canisters were collected) the precision was 1.69%. Two different laboratories had an absolute agreement of 8.9% and the sum-of-species from the gas chromatographic method was 2.4% lower than the principal laboratory total VOC from the PDFID method. The mean 6-9 am NMOC concentration over 22 cities was 0.756 ppmC.

These NMOC ambient data have been used in a number of EPA studies. One study computed the median ambient urban NMOC/NO_x concentration ratios for several US cities. These results are shown in Table 3-9. The median NMOC to NO_x ratio was 13.9 ppmC/ppm. Table 3-10 shows NMOC/NO_x ratios computed from the NAPAP 4.2 Emissions Inventory for a number of US cities. The median value was 3.9 ppmC/ppm. It is this type of discrepancy that strongly suggests that many NMOC sources may be missing in the current US inventories.

The gas chromatographic analysis of hydrocarbons in 772 canisters has been used for the purpose of producing chemical mechanism speciation, especially for use in the OZIPM/EKMA method[21]. As part of this analysis, the 20 species with the highest concentration in each canister were analyzed for frequency of appearance. Table 3-11 lists the 100 most frequently occurring compounds. Toluene appeared in the 20 highest concentration species in every canister. The 15th most prevalent species (1,2,4-trimethyl benzene) appeared in the 20 highest concentration species in 75% of all the

Table 3-9. Median Ambient Urban* NMOC-to-NO_x Concentration Ratios During 1984

EPA Region	Site	Ratio (No. of data)
III	Philadelphia	19.6 (45)
	Wilkes Barre	14.3 (53)
	Richmond	10.5 (62)
	Washington	9.4 (54)
IV	Memphis	13.9 (35)
	Chattanooga	16.8 (37)
	Charlotte	10.4 (55)
	Birmingham	11.7 (51)
	Atlanta	10.5 (52)
	Miami	13.3 (15)
	W. Palm Beach	14.3 (60)
V	Akron	12.8 (49)
	Cincinnati	9.1 (51)
	Indianapolis	8.3 (50)
VI	Beaumont	25.3 (45)
	Clute	23.7 (52)
	Dallas	16.0 (69)
	El Paso	15.3 (60)
	Fort Worth	11.6 (58)
	W. Orange	50.0 (41)
	Texas City	37.7 (52)
VII	Kansas City	-
Median of Medians		13.9 (21)

*In the Central Business District

Source: Richter, H. G., F. F. McElroy, V. L. Thompson, 1985: Measurement of Ambient NMHC Concentrations in 22 Cities During 1984. Paper 85-22.7, Preprint Volume, 78th Annual Meeting Air Pollution Control Association, Detroit, Michigan, June 16-21.

Table 3-10. NMHC/NO_x Emissions Ratios of Urban Counties

(Based on NAPAP 4.2 Emissions Inventory)

Urban Counties with Highest VOC Emissions Flux:

	County	Ratio
1.	New York, NY	3.15
2.	Queens, NY	3.93
3.	Baltimore City, MD	8.25
4.	Philadelphia, PA	3.70
5.	Richmond, NY	4.97
	Mean	4.80
	Median	3.93

Urban Counties with Highest NO_x Emissions Flux:

1.	New York, NY	3.15
2.	Hudson, NJ	1.49
3.	Queens, NY	3.93
4.	Union, NJ	2.91
5.	Philadelphia, PA	3.70
	Mean	3.04
	Median	3.15

Table 3-11. The One-Hundred Most Frequently Observed Hydrocarbons in 29 U.S. Cities

Total Number of Canisters = 773
Ave NMHC (ppbC) = 761.0 Max NMHC = 2764.6 Min NMHC = 175.7

Rank	Name	Mean	ppbC	Max	Min	Cans
1	TOLUENE	6.0%	45.4	18.7%	1.1%	773
2	n-PENTANE	3.7%	27.9	16.0%	0.8%	769
3	ISOPENTANE	7.4%	56.5	19.4%	0.7%	768
4	n-BUTANE	7.1%	54.3	22.4%	1.8%	766
5	m&p-XYLENE	3.3%	24.6	12.4%	0.6%	758
6	2-METHYLPENTANE	2.5%	19.1	5.6%	0.8%	753
7	ETHANE	4.4%	33.3	22.5%	1.1%	752
8	ETHYLENE	3.9%	29.1	30.3%	0.9%	746
9	BENZENE	2.2%	17.0	9.4%	0.7%	745
10	PROPANE	5.0%	37.6	25.6%	1.1%	739
11	3-METHYLPENTANE	1.8%	14.0	6.2%	0.7%	712
12	ISOBUTANE	3.3%	24.8	21.7%	1.1%	707
13	n-HEXANE,2-ETHYL-1-BUTENE	2.0%	15.8	8.5%	1.1%	678
14	ACETYLENE	2.6%	19.3	12.3%	0.7%	665
15	1,2,4-TRIMETHYLBENZENE	2.0%	14.8	7.4%	0.8%	647
16	o-XYLENE	1.5%	11.0	4.2%	0.7%	485
17	2,2,4-TRIMETHYLPENTANE	1.5%	12.1	2.4%	0.6%	420
18	PROPENE	2.1%	17.2	20.2%	0.8%	414
19	2-METHYLHEXANE	1.5%	11.3	3.4%	0.7%	379
20	p,m,o-METHYLSTYRENE	2.6%	16.3	15.8%	0.6%	306
21	2-METHYLPROPENE,BUTENE-1	1.5%	11.2	9.3%	0.7%	221
22	METHYLCYCLOPENTANE	1.4%	12.8	14.2%	0.7%	202
23	ETHYLBENZENE	1.6%	13.7	18.1%	0.9%	146
24	C10 AROMATIC	2.0%	9.7	5.4%	0.8%	128
25	3-METHYLHEXANE	1.4%	11.8	4.2%	0.8%	127
26	unknown	2.2%	14.4	15.0%	0.6%	123
27	C11 OLEFIN	2.0%	10.7	7.6%	0.6%	113
28	n-HEPTANE	1.3%	13.1	3.3%	0.6%	102
29	m-ETHYLTOLUENE	1.4%	10.3	2.5%	1.1%	99
30	2,3-DIMETHYLPENTANE	1.7%	14.3	3.6%	0.9%	76
31	1,2,3-TRIMETHYLBENZENE	4.1%	30.2	21.8%	0.6%	73
32	n-DECANE	1.7%	13.6	3.5%	0.8%	71
33	a-PINENE	4.9%	45.3	16.3%	0.9%	59
34	METHYLCYCLOHEXANE	1.3%	12.2	7.2%	0.7%	52
35	CYCLOHEXANE	3.2%	28.1	20.6%	0.6%	43
36	C8 PARAFFIN	1.7%	12.9	4.5%	0.7%	42
37	1-ME-4-ISOPROPYLBENZENE	2.3%	13.6	7.1%	0.9%	42
38	C6 PARAFFIN	2.9%	14.4	9.3%	1.2%	41
39	C9 OLEFIN	6.2%	53.4	13.6%	0.7%	39
40	C10 AROMATIC	2.4%	25.0	4.8%	1.0%	37
41	C11 AROMATIC	1.8%	8.8	5.6%	0.9%	33
42	C11 PARAFFIN	2.7%	10.4	11.5%	0.7%	29
43	2,2,3-TRIME-1-BUTENE	2.0%	14.7	8.3%	0.6%	26
44	C11 AROMATIC	1.9%	22.1	6.5%	0.8%	25
45	C10 PARAFFIN	2.8%	29.6	5.1%	0.9%	25
46	ISOPRENE	1.9%	8.8	6.0%	1.0%	25
47	c-2-PENTENE	2.0%	17.3	10.3%	0.9%	19
48	1,3-BUTADIENE	3.4%	22.7	10.4%	0.6%	18
49	C9 PARAFFIN	2.2%	17.8	12.6%	1.2%	18
50	1,2-DIME-3-ETHYLBENZENE	1.8%	12.2	3.8%	1.0%	18
51	n-NONANE	2.2%	17.9	5.4%	1.0%	17
52	C10 PARAFFIN	2.2%	25.1	0.1%	1.0%	17
53	t-2-BUTENE	1.5%	15.3	3.5%	0.9%	15
54	C10 AROMATIC	1.7%	19.8	3.3%	1.0%	15
55	C9 PARAFFIN	2.0%	10.3	3.1%	1.2%	14
56	n-OCTANE	3.4%	18.8	0.4%	1.2%	13
57	C6 PARAFFIN	2.0%	13.2	3.9%	1.2%	12
58	C10 PARAFFIN	1.8%	16.9	4.2%	1.1%	12
59	PARAFFIN	2.1%	9.3	6.3%	0.9%	12
60	UNKNOWN	9.8%	121.9	1.7%	5.5%	11
61	2,3-DIMETHYLBUTANE	1.4%	21.4	2.5%	0.8%	10
62	2-METHYL-2-BUTENE	2.3%	22.3	1.8%	1.0%	9
63	C3 PARAFFIN	3.5%	21.6	0.1%	1.2%	9
64	C7 PARAFFIN	2.4%	11.6	4.0%	1.2%	8
65	C5 OLEFIN	3.1%	31.9	8.9%	1.3%	8
66	2-METHYL-1-BUTENE	1.2%	9.3	2.0%	0.8%	7
67	t-2-PENTENE	2.4%	20.7	0.6%	1.0%	7
68	C10 PARAFFIN	1.7%	9.2	2.1%	1.1%	7
69	C7 PARAFFIN	1.7%	20.8	4.3%	1.1%	6
70	C6 OLEFIN	1.7%	12.8	2.8%	1.0%	6
71	C10 PARAFFIN	4.9%	31.7	7.7%	2.5%	6
72	C8 OLEFIN	1.5%	7.7	1.9%	1.3%	6
73	C6 OLEFIN	2.7%	26.6	8.7%	1.0%	6
74	ISOPROPYLBENZENE	3.1%	12.8	6.6%	1.2%	6
75	3,3-DIMETHYLPENTANE	2.3%	10.7	3.4%	0.7%	5
76	C10 PARAFFIN	2.7%	12.0	6.2%	2.0%	5
77	c-2-BUTENE	1.3%	17.4	1.8%	1.0%	5
78	C6 PARAFFIN	1.8%	11.7	3.4%	1.4%	5
79	C7 OLEFIN	1.7%	5.4	2.1%	1.3%	5
80	C6 OLEFIN	1.9%	16.0	2.4%	1.1%	4
81	C10 PARAFFIN	5.2%	31.9	8.7%	2.1%	4
82	C3 PARAFFIN	1.8%	21.4	2.4%	0.9%	4
83	CYCLOPENTANE	1.1%	15.1	1.7%	0.8%	4
84	delta-3-CARENE	4.4%	51.0	7.4%	1.4%	4
85	C8 PARAFFIN	1.2%	13.0	1.3%	1.0%	4
86	C7 PARAFFIN	1.5%	5.5	2.4%	1.1%	4
87	C11 PARAFFIN	1.1%	3.6	1.3%	0.8%	4
88	2-METHYL-2-PENTENE	2.4%	20.0	3.0%	1.6%	3
89	C5 OLEFIN	2.2%	8.2	3.1%	1.4%	3
90	C12 AROMATIC	1.7%	5.8	2.0%	1.2%	3
91	C10 PARAFFIN	3.7%	32.9	4.7%	1.4%	3
92	C9 PARAFFIN	1.6%	11.6	2.2%	1.5%	3
93	C12 PARAFFIN	1.4%	9.0	1.9%	1.1%	3
94	C9 AROMATIC	1.5%	12.5	1.7%	1.2%	3
95	c or t-2-HEXENE	3.8%	22.2	4.2%	3.2%	2
96	C12 AROMATIC	1.3%	6.3	1.5%	1.2%	2
97	2,2,5-TRIMETHYLHEXANE	1.1%	6.8	1.5%	1.0%	2
98	2,4-DIMETHYLHEPTANE	1.6%	3.6	1.7%	1.4%	2
99	C5 OLEFIN	3.3%	59.9	3.4%	3.1%	2
100	C4 OLEFIN	1.4%	15.7	1.5%	1.4%	2

canisters, the 25th most prevalent species (3-methyl hexane) appeared in 15% of the canisters, and the 50th most prevalent species (1,2-dimethyl-ethyl benzene) appeared in only 2% of the canisters. The aromatics toluene, m-xylene, and p-xylene and the C4, C5, and C6 alkanes dominate the top 10 species in the canisters. As will be discussed in a later section, these are the species for which the chemical mechanisms are the most uncertain.

4.0 CHEMICAL AND METEOROLOGICAL PROCESSES

4.1 Chemical Processes. Chemical Mechanisms and Models.

It has been established through numerous laboratory and field studies that photochemical ozone and other oxidants are products of atmospheric reactions involving organic pollutants (VOC), nitrogen oxides (NO_x) and sunlight. It is also established that the roles of the VOC and NO_x precursors in the mechanism of these reactions are so involved that only through complex kinetic mechanistic modeling is it possible to determine the magnitudes, and even the direction of the effects of precursor controls on ozone. Thus, photochemical kinetics models are indispensable in development of ozone control strategies. Chemical mechanism models must of necessity be simpler than the system they represent. Further, they can only include what is present knowledge of the actual chemical processes, and they well may include distorted representations of apparently known processes. Increases in computer resources have resulted in increases in the level of detail allowable in chemical mechanisms and still have them be feasible to solve; presumably a more detailed representation could lead to more accurate predictions. In addition, the continual increase in fundamental kinetics knowledge (the detection of new reactions, the measurement of their rate constants, and the elucidation of the reaction pathways of organic compounds) leads to a continual improvement in the accuracy of the model's representation and therefore to potentially better predictions for untestable conditions.

To prevent models from being the mere opinion of their developers, all models that have been used in regulatory applications in the US have had some evaluation against experimental data, usually smog chamber data. Interestingly, all model developers claim to have "fit the test data" reasonably well. For many of these models, however, subsequent laboratory research has revealed that many of the model's representations were incorrect and that they fit the test data because of various compensating errors in the mechanism, or because the test data were too few, or that critical input parameters for the test data were poorly known, or that the test data were simply too poor in quality to adequately exercise the weakest parts of the kinetics models or to be useful in distinguishing between two models with different representations. Thus, in the presence of such conditions, there has been a continual series of kinetics mechanisms "improvements", and, lagging somewhat behind these theoretical developments, there has been the production of experimental data to test and refine the mechanisms.

Because of the difficulties in testing perhaps imperfect mechanisms with perhaps imperfect data, and the desire for regulatory agencies such as the USEPA to select and use a single mechanistic model for computing control requirements, there is a need to improve the "process of mechanisms evaluation". Recognizing this need, the USEPA conducted a workshop in 1987 in which expert atmospheric photochemists and modelers discussed the different mechanism evaluation approaches and developed consensus conclusions on optimum approach as well as recommendations for additional research and development[22]. The participants agreed that while the comparison with theoretically explicit schemes and with field data approaches to mechanism

evaluation have merits, "evaluation against smog chamber data provides the most unambiguous test of urban atmospheric photochemical mechanisms". They also agreed, however, that there are uncertainties associated with the smog chamber data. For example, there are uncertainties associated with the representation of chamber radical sources and of photolytic rates in outdoor chambers, with smog chamber measurement errors, and with the representation of as yet unknown reaction pathways.

European investigators also agreed that it is important to ensure the fullest possible testing of the chemical mechanisms against smog chamber data. They also feel, however, that a further evaluation stage is required which has been shown in Europe to be invaluable in providing policy guidance for the ozone problem. This involves evaluation against a benchmark chemical scheme in a quasi-realistic scenario application. This evaluation has been performed using complete and condensed versions of schemes, to provide benchmark secondary pollutant concentrations and chemical reaction flux diagnostics. These will have a vital role to play in the subsequent evaluation of control strategies determined from applications of the schemes within large integrated modeling studies.

Today's situation is that mechanisms suitable for regulatory use contain three types of reactions:

1) The first class of reactions are those which are well characterized by the kinetics research community and appear in major reviews such as those published by the NASA, CODATA, and IUPAC Groups. At present these include about 360 reactions which are mostly inorganic, but there are data sheets on organic reactions for molecules up to three carbons. All acceptable chemical kinetics mechanisms include the most important of these reactions at their consensus rate constants. The different chemical mechanisms are essentially identical for this portion.

2) The second class of reactions are those which are known to occur and for which subsequent reactions of the products are fairly well characterized, but for which absolute rate constants are unknown. Thus, acceptable chemical kinetics mechanisms will include these reactions, but may have different rate constants, resulting in the same products being formed, but at different rates and magnitudes. "Model tuning" to experimental data is often used to select these parameters. The C3+ olefin reactions and C6+ alkanes are in this class.

3) The third class of reactions are those which are known to occur, but for which the subsequent reactions after the initial one are essentially unknown. Thus, chemical kinetics mechanisms will include the first reaction at a consensus rate, but subsequent reactions and rates are based on the beliefs of the mechanism author. Therefore, not only are the parameters in the reactions the result of "model tuning", the whole reaction scheme is produced this way. All of the reactions of aromatic compounds are in this class.

In addition to these classes of reactions, to deal with the complexity of the hydrocarbon chemistry, two different methods for generalizing their chemistries have evolved: the "lumped molecule" or surrogate species approach, and the "lumped structure" or carbon bond approach. In the former, the nearly explicit chemistry of a particular molecule is chosen to represent the chemistry of an entire class of compounds, i.e. propene may represent all terminal olefins. Carbon number differences are ignored when molecules are assigned to surrogates. In the latter, each molecule to be represented is broken into different model species such that all the carbon is accounted for. The model species are organized around carbon bond types. In this scheme, propene would be assigned to two model molecules: to OLE, which is a two-carbon double bond entity, and the terminal carbon on propene would be assigned to PAR, which is a single carbon entity. Carbon concentration is conserved in the latter. In actual practice, each kinetics mechanism uses a combination of methods to represent the complex urban hydrocarbon mix.

Presently, the mechanisms most comprehensively evaluated against smog chamber data are the latest versions of the Carter, Atkinson, Lurmann (CAL) mechanism[23] and the Carbon Bond (CB4) mechanism[24]. The CAL mechanism is a 132-reaction step scheme that uses the "lumped-molecule" approach. The CB4, an 81-step mechanism, uses a "lumped-structure" approach. Other pertinent distinguishing characteristics of the two mechanism are summarized in Table 4-1.

The CAL mechanism was evaluated by comparing mechanistic predictions of ozone yields with yields observed in smog chamber irradiations of a variety of VOC, NO_x mixtures. The smog chamber data used were obtained from some 490 experiments carried out in three indoor and outdoor chambers of the Statewide Air Pollution Research Center, U. California/Riverside, and one outdoor dual chamber at the U. North Carolina/Chapel Hill. A comparison of CAL-predicted and CB4-predicted maximum ozone concentrations with concentrations observed in the smog chamber is shown in Figure 4-1. Both mechanisms' predictions agree with the smog chamber data within 30% (with a few exceptions), a performance which at first glance appears quite satisfactory. Such comparisons, however, are not of unquestionable validity.

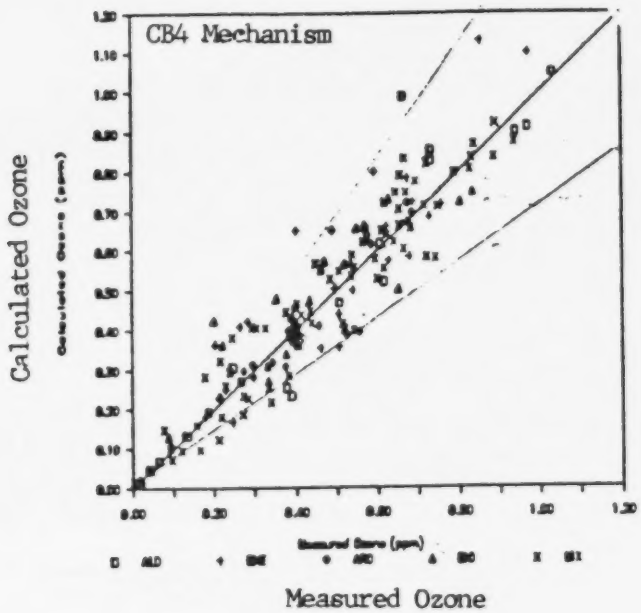
These evaluations were done independently by the respective model developers, using somewhat different sets of smog chamber data and different evaluation procedures. They used different assumptions regarding light characterization, chamber effects, and in some cases different sets of rate constant values. The mechanisms have different parameters for the yields of radicals and products for propene and differ significantly in their description of aromatics oxidation pathways. In addition, the mechanism tests ignored the side-to-side test conditions in the UNC dual chamber, i.e. performances were assessed independently for each side, even though the data were paired.

Table 4-1. Characteristics of the CB4 and CAL Mechanisms for Ozone

Characteristics	CB4	CAL
Mechanism Type	Lumped Structure	Lumped Molecule
Number of Reactions	81	132[a]
Inorganic Reactions	30	29
Organic Reactions	40	86
Photolytic Reactions	11	17
Number of Species	34	51
Inorganic Species	15	15
Primary Organics[b] or bonds representing ambient VOC mix	9	12
Alkanes	1	2
Alkenes	2	3
Aromatics	2	3
Biogenic VOCs	1	-
Aldehydes	2	3
Non-Reactive VOCs	1	1
Organic Products	4	13
Organic Radicals	6	11

[a]Includes pseudo-first-order reaction to represent methane oxidation with a global methane concentration of 1.85 ppm

[b]Organics or bonds for which either emissions or initial conditions should be specified



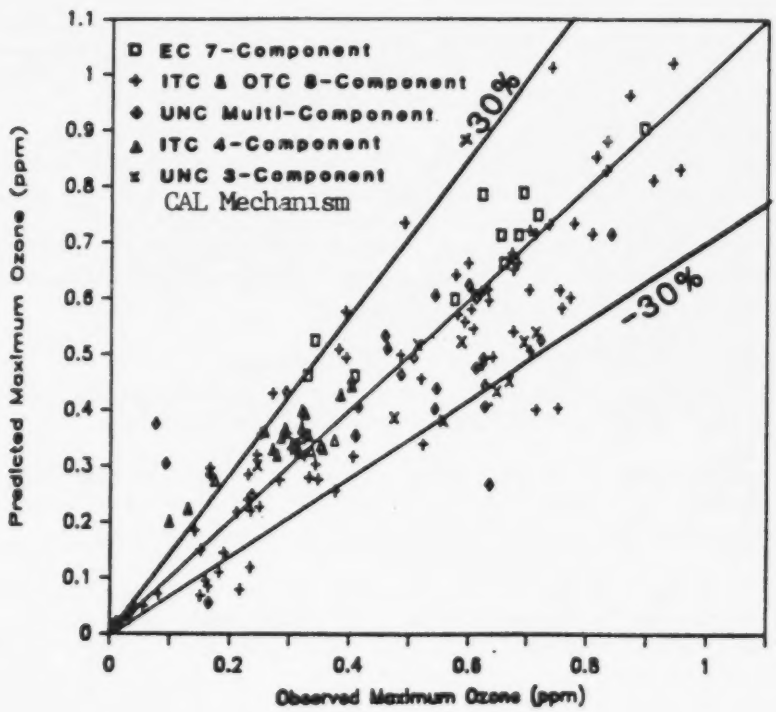


Figure 4-1. Scatter diagrams comparing model-predicted maximum ozone concentration versus measured values in several smog chambers

Following the developers tests, a comparison and test of the two mechanisms using selected UNC chamber data and uniform sets of input parameters and conditions was carried out at UNC[25]. The first step was to reconcile the different rate constants each mechanism used for the inorganic and carbonyl chemistries. Then a detailed characterization of the actinic flux in the outdoor chamber was used to re-specify the photolytic rates used in both mechanisms. Finally, a comparison of different methods for representing the chamber background reactivity was conducted. The mechanisms were then exercised over a series of "hierarchy of species" tests. Using exactly the same inputs to each mechanism, the results for NO_x, O_3, and the principal HCs were that:

a) Both mechanisms were in excellent agreement with each other and with data for formaldehyde-NO_x experiments;

b) Both mechanisms were in very good agreement with ethene until the very end of the experiment where the reactivity of CAL decreased slightly compared to the data and to CB4; this decrease in CAL was due to different radical termination chemistry than CB4;

c) CAL was in better agreement with propene experiments than CB4 which was too reactive due to a higher radical yield in the ozone + propene reactions;

d) Both did poorly for 1-butene experiments;

e) CAL was significantly better at simulating t-2-butene experiments than was CB4; this is because CAL has an explicit representation for t-2-butene and CB4 uses two ALDs as a surrogate representation which results in very slow initial chemistry in CB4;

f) CB4 was significantly better at simulating toluene experiments; CAL was significantly better for xylene;

g) Both mechanisms often did better at simulating mixtures of hydrocarbons with all classes present than they did simulating the individual components of the mixtures;

h) Both mechanisms simulated a 16-component synthetic automobile exhaust mixture experiment very well, including the effects of replacing 1/3 of the mixture carbon with methanol;

i) Both mechanisms were uniformly too reactive for synthetic urban hydrocarbon mixture (18-components) experiments although the ethene, propene, and toluene decays were well fitted;

j) Neither mechanism did well for cool conditions and neither mechanism predicted formaldehyde as a product very well, being too low in the olefin systems and too high in the aromatic systems.

The conclusion from this comparison study was that while the two mechanisms sometimes differ in comparison with chamber data, in many cases, neither is superior to the other. Much of the difference between the mechanisms arises from the differences in "model tuning" against chamber data which was used by the developers to estimate the parameters in the olefin and the mechanistic pathways and parameters in the aromatics chemistry. These choices become confounded with the choices made for photolytic rates, that is, the light characterization of the chambers, and with the choice of wall radical representations, that is, with the quality of the chamber characterization and its representation. While the use of more uniform assumptions could narrow the difference between the two mechanisms, real advancement in mechanism quality awaits improved kinetics data on rate constants and pathways for secondary reactions. Improvements in the data would result from a mechanistic understanding of chamber radical sources.

This issue of proper evaluation of chemical mechanisms was discussed exhaustively in USEPA's 1987 Workshop on Mechanism Documentation and Evaluation[22]. One key recommendation arrived at by the participants--and endorsed in this Workshop--was that several review groups be established for the purpose of periodically assessing the state of knowledge and establishing consensus opinion in several domains, namely: accuracy of kinetic data, validity of mechanistic pathways, quality of smog chamber data, and mechanism evaluation (against smog chamber data) protocols. With the exception of kinetic data accuracy, no such review activities are currently in existence. With respect to kinetic data evaluation, two review panels have been in existence for the past 12 years: a NASA panel and a CODATA Task Group. The NASA panel has produced at regular intervals a total of eight reports containing evaluated data on approximately 200 thermal and photochemical reactions. The CODATA Task Group, recently replaced by an IUPAC sub-committee has just completed its fourth evaluation which now includes data sheets for 360 reactions of atmospheric interest, including organic molecules containing up to three carbon atoms. Such an evaluation, which involves detailed assessments of the laboratory studies along with estimations of error limits is clearly an excellent starting point for considering a detailed mechanism for the formation of photochemical oxidant in the troposphere.

It is doubtful, however, in terms of the long time scale for detailed kinetic data evaluation, if the present efforts of these panels will ever reach the point of including a reasonably complete set of evaluated data for the enormous range of possible reactions in the polluted troposphere. It is likely that future evaluations by the IUPAC sub-committee, in particular, will be expanded by including assessments of only key reaction types for the more complex organic species.

To fill the present gap between the individual reaction approach of the evaluators and the detailed mechanistic requirements of the atmospheric modellers, it would be desirable to set up an international panel with the task of preparing a consensus mechanism for tropospheric photo-oxidative degradations or organic species in the NO_x polluted troposphere.

4.2 Meteorological Processes. Pollutant Transport and Dispersion/Transport Models

The distribution of chemical constituents emitted into the atmosphere is critically related to the vertical and horizontal transport. The mechanisms for vertical exchange are complex and varied, ranging from clear-air processes over various terrain and land use conditions to moist convection associated with non-precipitating clouds and cloud systems. Precipitating clouds redistribute pollutants vertically in the atmosphere, with updrafts carrying surface-based pollutants into the upper layers, and downdrafts bringing both rain and cloud and interstitial air to the lower levels of the earth's surface. With regard to photochemical oxidants, non-precipitating clouds are of particular interest, since they are prevalent in the warm season and are effective in redistributing pollutants between the mixed layer and the free troposphere. The magnitude of their impact is highly variable in time and space and will depend on the cloud population, distribution and their vertical extent. Entrainment processes within the clouds play a critical role in determining the net vertical exchange in the atmosphere. The horizontal distribution and population density of clouds are highly variable regionally and over diurnal and seasonal time scales. Long range horizontal transport of ozone and its precursors are expected to be strongly influenced by cloud systems. Experimental evidence of cloud-induced vertical exchange of ozone between the mixed layer and free troposphere has recently been documented[26].

Horizontal transport of pollutants on a regional scale is controlled by the height at which emissions are released, their chemical and physical lifetimes and horizontal dispersion. Consequently, the horizontal distribution of pollutants is strongly impacted by such factors as the speed and direction of the transport winds, vertical mixing in and between layers, presence of wind shear, extent of coupling between the mixed layer and the free troposphere, surface pollutant fluxes and source distribution. The transport winds are expected to translate along isentropic surfaces, which are not necessarily horizontal. Wind shear will cause pollutant sources to undergo horizontal transport and dispersion such that the pollutants in the upper air will be redistributed in three dimensions and over a greater area than would be otherwise anticipated from surface winds. Significantly, distorted horizontal patterns will develop and vary with respect to the vertical levels of the atmosphere and the varying transport and dispersion conditions.

Simulation of the atmospheric transport in photochemical grid models (e.g. the Systems Applications, Inc. Urban Airshed and Regional Transport Models; the EPA Regional Oxidant Model) requires input to the model of horizontal wind vectors defined at each model grid point, usually on an hourly basis. (The models themselves compute vertical velocity via a form of the mass continuity equation.) Techniques for wind field generation can be divided into three general classes:

objective analysis of observational data

diagnostic wind modeling

prognostic meteorological modeling

In general, the choice of technique depends on the spatial and temporal representativeness of available observational data.

Objective analysis involves the mathematical combination of observational data to produce a wind vector at a given grid point. Objective analysis encompasses both interpolation and extrapolation, depending on the location of the grid point with respect to the location of available observations.

Use of objective analysis techniques to generate gridded wind fields for a photochemical model implies an assumption that available observations completely represent the airflow within the model domain. This assumption is frequently of doubtful validity, especially in regions of complex terrain where the spatial separation between wind observations is much greater than the relevant terrain scales.

Diagnostic wind models provide relatively simple representations of certain complex terrain effects on airflow, including deflection of airflow by terrain obstacles and thermodynamically generated slope flows. The diagnostic models generally combine the terrain-effect treatments with objective analysis of available observations. In one approach, an objective analysis of observations is carried out; the objectively analyzed field is then adjusted for terrain effects. In a second approach, a "first guess" wind field is generated by adjustment of "mean" flow for terrain effects. The "first-guess" field is then incorporated along with available observational information into an objective analysis, with the "first-guess" field weighted heavily in subregions of the domain remote from observations.

Diagnostic wind models are relatively inexpensive to run and in certain areas may require fewer observations to produce credible wind fields. However, diagnostic wind models are incapable (in the absence of representative observations) of generating such airflow features as sea breezes, low-level jets, and terrain-generated mesoscale eddies. Representation of such features may be important for accurate air quality simulation.

Both objective analysis and diagnostic wind models rely on observational data as critical inputs. Observational data are irregularly distributed in space, and in general, are not available in one-hourly intervals. They have to be analyzed objectively on a regularly spaced three-dimensional grid and interpolated in time. Standard methods are available to interpolate primary meteorological variables as wind or temperature, but problems arise in interpolating cloud cover or precipitation rates. The 12-hourly precipitation rates from the international observational network are not sufficient for input to episodic models. Also, cloud top heights are not available from the conventional synoptic network. These gaps could be

filled partly by using satellite and radar data. Unfortunately, these data are not available in a form to be used directly as input for a grid model. Extensive data processing and interpretation are necessary to extract the desired information. It is possible to derive variables such as the height of cloud tops, cloud cover and cloud type from such data, but at this time the methods needed are still under development and not applicable routinely.

The third category of wind field generation, prognostic mesoscale meteorological models, provides numerical solutions of the governing equations of the atmosphere. Unlike objective analysis and diagnostic wind modeling, prognostic models do not require significant mesoscale observational data inputs. Given (1) a representation of the initial dynamic/thermodynamic state of the atmosphere within the model domain, and (2) a representation of the "forcing" of domain-scale flow by larger-scale processes not simulated by the model, the prognostic model simulates the response of the mesoscale airflow to differential surface heating (e.g. sea breeze circulations) and to complex terrain (e.g. thermodynamically-generated slope flows, blocking and deflection of airflow by terrain obstacles, mesoscale eddy development).

The major advantage of prognostic modeling over the other two methods is the ability of prognostic models to simulate relevant physical processes in the absence of mesoscale observational data. This may be especially important in representing the spatial and temporal variability of upper-air (i.e. above, say 100 m AGL) winds for which representative observations are frequently sparse or unavailable.

In addition to simulating the wind field, prognostic models simulate the temperature field. Thus, prognostic models may be capable of providing necessary mixing height and stability information to photochemical grid models.

The major disadvantage of prognostic modeling is its computational expense relative to other methods of wind field generation. Additionally, prognostic models cannot be expected to reproduce all available individual wind observations. If, for example, the location of frontal systems, cloud and precipitation patterns, or the wind field are incorrectly forecast, it cannot be expected that the predicted pollution coincides with measurements. Therefore, if a dynamical model is used as a driver for a complex dispersion model, it is necessary to perform a comprehensive meteorological analysis utilizing all available observations in order to estimate the uncertainty in the predicted meteorological variables.

In the framework of the PHOXA program both methods have been used to prepare meteorological input for complex dispersion models. The application of an episodic photochemical model for the simulation of three photochemical episodes in north-western Europe has shown that model results are quite sensitive to the meteorological input, i.e. an accurate description of meteorological input fields is a necessary premise for good model performance.

Major problem areas in the preparation of the meteorological input for the RTM-III have been:

- Wind fields over the sea. In Europe during the air pressure configurations, usually associated with oxidant formation, pollutant transport occurs quite often over the sea, e.g. between the continent and the UK, or between the UK and Scandinavia. Lack of data makes it difficult to determine accurately the respective transport winds.

- Sea breeze circulations. The significant temperature differences between land and water establish land-sea-circulations which lead to a cycling of primary and secondary pollutants. Available data and the grid size used in the regional modeling make it difficult to consider such effects.

- Mixing heights. The height of the boundary layer determines the vertical extension of the first transport layer of the RTM-III, the mixed layer. Mixing heights for RTM-III are constructed from observational data in connection with a boundary layer model. In particular, the calculation of the vertical extension of the ground-based nighttime inversion is fairly inaccurate. There are also problems in the transition area between land and sea where internal boundary layers can develop.

5.0 MODELING TECHNOLOGY AND APPLICATIONS

5.1 Physicochemical Air Quality Models

Physicochemical air quality simulation models (AQSM) are now accepted as being the most effective tools for development of ozone control strategies. Such models have been in existence in the US for the past two decades, but it is only recently that AQSM's have been put to routine use in activities pertaining to assessment, management and reduction of ozone risks. The models most commonly used currently in the US are the Empirical Kinetic Modeling Approach (EKMA) model[27,28], the Urban Airshed Model (UAM)[29] and the Regional Ozone Model (ROM)[30]. The USEPA-developed EKMA model was conceived as and intended to be a mathematical expression of the causal relationship between reactants and products in the O_3-forming process, for given sunlight intensity and temperature conditions. The model treats the entire urban atmosphere as a reaction vessel, and is used in the form of O_3-isopleth plots depicting dependence of peak O_3 concentration in the urban area on 6-9-am concentrations of NMHC and NO_x. The effect of post-9-am emissions is considered by assuming such emissions to disperse uniformly in the mixing layer above the urban area. Precursors and O_3 transported into the urban area, also, can be taken into account using some simplifying assumptions. The EKMA model is not intended to predict absolute O_3 concentrations; rather, it is intended to predict changes in peak O_3 concentration as a function of changes in the precursor concentrations and/or emissions. This is a conceptual weakness of the model because it makes it extremely difficult to evaluate the model's accuracy using real world data. Relative to UAM and ROM, EKMA is the simplest model and is appropriate for use only in the uncomplicated case of O_3 arising at the end of the day from emissions within an isolated urban area. For complex cases, such as when the O_3 problem results from multi-day pollutant transport or from rural emissions or when the transported-in pollutants dominate the O_3-forming process, the EKMA model is inappropriate[31]. Nevertheless, because of its simplicity and low application costs, the EKMA model found considerable use in regulatory activities in the US.

The SAI-developed UAM model is a grid-type model with four vertical layers and grid size from 1 Km to 10 Km. It can treat all major physical and chemical processes underlying the photochemical ozone formation, namely, advection, diffusion, deposition and chemical transformations of emissions. Because of this the UAM is capable of predicting absolute O_3 concentations, an advantage over EKMA in that it allows for field evaluation of the model. For the same reason, the UAM is inherently more valid than EKMA but is also much more complex. It is also costly to use because of the extremely detailed emissions and meteorological data required as input to the model. Like EKMA, UAM also is an urban scale model that predicts O_3 concentrations resulting from a single day's reaction of the urban areas emissions. It is clearly the more appropriate model to use in urban areas with complex photochemical O_3 problems[31]. All input information required by both EKMA and UAM is available or can be measured except for future boundary conditions (i.e. concentrations of O_3 and precursors at the boundaries of the models' domains). The requisite data on this latter input can be estimated only through use of predictive regional scale models such as the ROM.

The USEPA-developed ROM model is a grid-type model with 3 1/2 vertical layers and 18 Km grid size. It was designed to treat all processes known to affect ozone formation during several days or ~1000 Km of pollutant transport, namely, advection, photochemistry, nighttime chemistry and transport, pollutant "venting" through cumulus clouds, mesoscale vertical motion and eddy effects, terrain effects, subgrid scale chemistry processes, natural emissions chemistry and transport, and wet and dry deposition. The model was developed mainly for the purpose of perdicting future impacts of upwind sources on an urban area's air quality. Thus, it is ideally suited for implementing the regional approach to developing urban O_3 control strategies. The complexity of the model and cost of application, however, limit seriously the model's utility. To illustrate the magnitude of the modeling effort associated with applications, a three-day simulation requires six hours of an IBM 3090 computer as well as 25 mandays and 15 hours of a VAX 785 computer for data preparation and quality assurance. Also, the probabilistic nature of the model predictions complicates the use of ROM for O_3 strategy development. Notwithstanding all these difficulties, however, the ROM is already extensively used in the US and promises greater use in the future.

5.2 Applications of AQSM's

Numerous AQSM application studies have been conducted in the US by Federal, State or local government agencies, research institutions and model developers. Most common objective in those studies was to study the relative roles of VOC and NO_x in the photochemical O_3 problem and determine and compare impacts on O_3 air quality of various unilateral or combined VOC and NO_x control strategies. As a result of these studies, the USEPA has recently rescinded its long standing policy that O_3 must be controlled through unilateral control of VOC, and is now receptive to O_3 reduction strategies based on NO_x control. The most significant findings from those studies are listed in Table 5-1 in the form of observations arrived at through use of the EKMA, UAM and ROM models.

Generally, the modeling studies to date appear to suggest that relative to NO_x control, VOC control is the more effective approach to urban O_3 reduction. Existing models, however, still have imperfections and, also, the issue of whether or to what degree biogenic emissions influence the VOC-to-NO_x ratio in urban areas generally, has not been resolved yet.

A large number of photochemical model application studies have been performed within Europe also, on various aspects of the ozone problem. A wide variety of approaches have been adopted to account for dispersion and transport including single layer long range transport trajectory models, urban scale trajectory models and large scale grid models. The chemical schemes vary from extensive schemes involving over 300 reactions through to the highly condensed acid-parameterized schemes associated with grid models. Common themes recur in all these applications; hydrocarbon controls always reduce ozone whereas nitrogen oxides controls always increase ozone in some places and decrease ozone in other places. Also, a framework of emission control scenarios incorporating Best Available Control Technologies have been analyzed showing the importance of controlling some source categories and the relatively smaller impact of controlling others.

Table 5-1. Summary of Modeling Results Concerning Effectiveness of VOC, NO_x, and Combined Strategies for Reducing O_3

Observation	Model(s)
1. NO_x decrease increases O_3 near sources of NO	EKMA, UAM, ROM
2. NO_x control reduces peaks, but may move them closer to cities	UAM
3. With "high" NMOC/NO_x ratios (e.g. >10:1) reductions in peak O_3 accompanying initial control efforts may be more pronounced with NO_x controls than for VOC controls	EKMA
4. Despite more rapid initial reduction in peak O_3, ultimate efforts needed to attain an air quality goal may sometimes be greater for NO_x control than for VOC	EKMA
5. Greater benefit of NO_x control appears far downwind of urban areas (where O_3 formation is presumably NO_x-limited)	EKMA, UAM, ROM
6. Undesirable effects in #1, 2, 4 may be reduced or sometimes eliminated by controlling <u>both</u> VOC and NO_x	EKMA
7. Increases in O_3 due to NO_x control occur in urban commercial districts where O_3 is relatively low (Note: ROM results show this result as well as showing O_3 increases in the vicinity of high concentration areas near major urban source regions. This could reflect ROM's coarser spatial resolution or UAM's limited ability to consider transport from upwind sources.)	UAM
8. VOC controls work by delaying or slowing down O_3 accumulation	EKMA
9. VOC controls reduce peak O_3 and move the reduced peaks further downwind	EKMA, UAM, ROM
10. Greatest reduction in O_3 accompanying VOC controls occurs in major source areas, with reductions being somewhat less far downwind	EKMA, UAM, ROM
11. With "high" NMOC/NO_x ratios (e.g. >10:1) effect of initial increments of VOC control may be small	EKMA

Observation	Model(s)
12. NO_x or VOC + NO_x control becomes preferable to controlling VOC alone as	EKMA
a. NMOC/NO_x ratio increases	
b. severity of observed O_3 levels decrease	
c. reactivity of VOC emissions increases	
d. atmospheric dilution increases	
13. NO_x controls could lower population exposed to peak O_3 levels but raise population exposed to moderate levels	UAM
14. The variation of VOC composition as described in Section 3.2.4 was found to have less than 10% effect on VOC control requirements for both the CB4 and CAL mechanisms	EKMA

Note: UAM results reflect use of CB2 chemical mechanism.
EKMA results reflect use of CB3 chemical mechanism.
ROM results reflect use of CB4 chemical mechanism.

* EKMA: Empirical Kinetic Modeling Approach, trajectory model on the urban scale, vertical resolution is mixed layer average

UAM: Urban Airshed Model, three-dimensional grid model on the urban scale

ROM: Regional Oxidant Model, three-dimensional grid model on the regional scale (1000 km)

6.0 SCIENTIFIC ISSUES ASSOCIATED WITH O_3 CONTROL STRATEGIES

Despite decades of research in several countries on all aspects of the photochemical O_3 problem, scientific issues still persist and, apparently, hamper the O_3 control effort seriously. Evidence on existing scientific issues has been provided on an issue-by-issue basis by researchers and also collectively by the fact that apparent emission changes have not impacted O_3 air quality in accordance with theoretical expectations. The experience in the US, for example, is that despite the substantial VOC controls effected in past years the O_3 air quality standard of 0.12 ppm for 1 hr/year continues to be unattainable in most urban areas. The USEPA viewpoint on this O_3 non-attainment problem is that while unresolved scientific issues are a part of the cause, most of the problem is probably due to uncontrolled and unpredicted emissions growth that partly or more than offset the emissions reduction due to controls. Critics of the USEPA policies, on the other hand, allege that while all reasons for the non-attainment problem are not clear, at least one cause of the problem is that the US control policy is based on inadequate, if not wrong, understanding of the photochemical O_3 formation process and the factors affecting it.

As already discussed, well established scientific issues exist within the chemical mechanism area, namely: the mechanisms of the atmospheric reactions of the aromatic VOC's and the large molecular size VOC's are not known accurately. Also, uncertainties exist in the photolytic roles of certain important carbonyls (e.g. formaldehyde, glyoxals, ketones). There may be other inaccuracies that escape detection because the methods for evaluating chemical mechanisms and kinetic parameters of the involved reaction steps have not been perfected yet. Thus, evaluation of mechanisms through comparisons with smog chamber data is still obscured by the fact that chamber walls cause "extra reactivity" the origins of and methods for accounting for which have introduced uncertainties in predictions. Errors are also likely to be introduced by errors in the chemical composition of the ambient VOC mix--an important input to mechanistic models. Errors of this type are most likely to occur in the measurements of oxygenated and large molecular size VOC's.

In the EKMA modeling area, the next most important issue is the selection of the VOC-to-NO_x ratio value to be used as input to the model. Measurements of the 6-9-am ratio in center city areas give highly varying (with time and location) results and no bases have been found yet for justifying selection of e.g. the average or the median or any other single value for the ratio.

In the emissions disperison area, the most important issue probably is the one associated with the accuracy of the emission inventory data currently available. There is considerable evidence that the US emission inventories for VOC are underestimated in some cases because sources have escaped inventorying and in other cases because emission rates have been underestimated. Use of underestimated VOC emission inventory data would result in artificially low VOC-to-NO_x ratio conditions which, in turn, would make the models overpredict the effectiveness of VOC control or underpredict VOC control requirements. A similar effect and error may be caused by ignoring the biogenic VOC emissions in urban ozone control strategies.

These as yet unresolved issues have cast doubts on the reliability of the current air quality models, not only for computing control requirements, but also for determining whether, relative to NO_x control, VOC control is the more effective approach to O_3 reduction. With respect to the roles of these scientific issues in the O_3 non-attainment problem, the US experiences have been used to support three distinct viewpoints. The USEPA viewpoint, adhering to the air quality management approach to combating air pollution, favors continuing confidence in current scientific knowledge and models. As its post 1987 ozone policy, USEPA continues to favor VOC control for O_3 reduction but is now receptive to strategies that include NO_x control for achievement of the O_3 standard. An opposing viewpoint, expressed within the industrial scientific community, holds that current understanding of the ozone problem is seriously lacking and that triggering of the photochemical ozone-forming process by photochemically aged pollutants and by stratospheric ozone are not properly considered in the theory currently accepted and used by USEPA. Finally, the viewpoint held by some State of California air pollution analysts is that state-of-the-art models are not reliable enough to be used for development of quantitative control strategies; they should be used instead only for making general or qualitative judgments about effects of emission controls or of other factors on air quality. Others, such as the South Coast Air Quality Management District, are making comprehensive use of three-day simulations with an enhanced version of the Urban Airshed model.

7.0 CONCLUSIONS AND RECOMMENDATIONS

1. Photochemical O_3 problem arises from atmospheric reactions of VOC and NO_x emissions under favorable sunlight intensity, temperature and dispersion conditions. Such conditions occur frequently both in the US and Europe as suggested by the O_3 monitoring data available for urban and rural areas in the two continents. Such data indicate hourly O_3 concentrations as high as 0.3 ppm to occur in Europe and even higher in the US.

2. The dual roles of VOC and NO_x, being both precursors and scavengers of ozone, make the photochemical O_3 formation process so complex that effective ozone control strategies cannot be developed based on common sense alone. Accurate ozone air quality models are required, which, in turn, requires that the processes of emission, dispersion and chemical reaction of ozone precursors in the atmosphere be understood in detail and quantitatively. These processes have received in the past years considerable research attention both in the US and Europe but significant gaps and scientific issues are still in existence. The seriousness and apparent intractability of the photochemical ozone problem make it imperative that research continues toward resolution of the scientific issues and that the research efforts in the European countries and the US be coordinated to the extent possible for maximum effectiveness.

3. Precursor emission rates are the single most important factor to consider in development and implementation of ozone control strategies. Substantial efforts have been expended both in Europe and the US for development of accurate VOC and NO_x emissions inventories. Considerable uncertainties, however, continue to exist especially in the levels and composition of VOC emissions. Particularly disconcerting are errors causing underestimation of VOC emissions because such errors also lead to overestimation of the effectiveness of VOC controls for O_3 reduction. Crucial uncertainties are associated also with the biogenic VOC's, both in regards to their emission levels and also in regards to the importance of their role in the chemistry with respect to destruction and formation processes of tropospheric ozone.

4. Atmospheric dispersion and transport processes are of particular interest both because of their direct connection to the magnitude of the ozone problem and also because of the political implications of inter-country or inter-state pollutant transport. This emphasizes the need, both in Europe and in the US, for regional scale ozone models capable of determining source area-to-receptor area and ozone-to-precursor emissions relationships in a quantitative and reliable fashion.

5. Significant advances have been achieved in the recent years in the atmospheric chemistry underlying the photochemical ozone problem. Atmospheric reaction pathways have been established for most ambient VOC's and reaction rate constant values for a significant number of atmospheric reaction steps are of undisputed validity. Gaps of strong consequence, however, still exist, particularly in the aromatic VOC

chemistry area and perhaps in other, unsuspected areas as well. With respect to this latter possibility, it is crucially important that methods be developed for reliably and accurately evaluating chemical mechanisms and identifying sources of error. Given the importance of the existing gaps and issues and the substantial relevant expertise lying within many countries in the world, it would be extremely productive to promote international collaboration among experts in the atmospheric reaction mechanism, kinetics, and chemical modeling areas.

6. Ozone air quality models are now available and in routine use both in the US and Europe. Modeling studies to date established that the ambient VOC-to-NO_x ratio condition is extremely important in that it determines whether VOC control or NO_x control is the more effective approach to ambient O_3 reduction. The models indicate specifically that low VOC/NO_x conditions favor VOC control whereas under high VOC/NO_x conditions NO_x control is the more effective approach to reducing peak O_3 concentrations. While the quantitative aspects of the ozone-precursor dependencies derived by models are uncertain reflecting the uncertainties in the model and model inputs used, the qualitative aspects and, in particular, the directional effects described above of precursor controls on ozone for high and for low VOC/NO_x conditions, are almost certain to be accurate, unaffected by current model imperfections. This underscores the importance of the VOC/NO_x input to the models and, hence, the need for reliable estimation of the VOC and NO_x emission and ambient concentration factors.

7. Based on the conclusions from the Workshop discussions and on impressions from interactions among the Workshop participants, the Workshop Steering Committee submitted the following specific recommendations for future actions:

   (a) The results of this Workshop should be reported to the Coordinators of the US-German Environmental Program, and that work on the photochemical ozone problem and related issues be recognized and continued as a Project activity under the US/FRG Environmental Agreement, with Dr. Basil Dimitriades, USEPA, and Mr. Erich Weber, FRG/BMU, as the respective US and FRG Co-Chairmen.

   (b) Support should be provided by the US and FRG Governments for the organization and conduct of the Second US/FRG Workshop on Ozone in FY-90 (i.e. Spring 1990).

   (c) A program should be sponsored within the US/FRG Environmental Agreement for facilitating/supporting exchange of scientists between US and FRG for a three to six-month duration.

   (d) International Work Groups should be formed under joint US/FRG sponsorship to perform critical reviews and assessments of:

      (i) State-of-the-Science chemical mechanisms for ozone

      (ii) Existing smog chamber data bases

(iii) Existing reaction rate constants

(iv) Development of advanced analytical techniques applicable for field as well as for smog chamber studies

(v) Research needs in the area of ozone problems in general.

The Work Groups should convene in conjunction with the Second US/FRG Workshop on Ozone.

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LIST OF PARTICIPANTS

Monika Baer
Institut für Meteorologie
und Klimaforschung
Kernforschungszentrum
Karlsruhe/Universität Karlsruhe
Postfach 3640
7500 Karlsruhe/FRG
Tel. (7247)824770

Volker Bastian
Universität Wuppertal
Phys. Chemie, Fachbereich 9
Gaußstr. 20
5600 Wuppertal/FRG
Tel. (202)439-2510

Karl H. Becker
Universität Wuppertal
Phys. Chemie, Fachbereich 9
Gaußstr. 20
5600 Wuppertal/FRG
Tel. (202)439-2666

Frank Black
Atmospheric Sciences Research Laboratory
US Environmental Protection Agency
Research Triangle Park, NC 27711/USA
Tel. (919)541-3037

Thomas C. Curran
Office of Air Quality Planning and Standards
US Environmental Protection Agency
Research Triangle Park, NC 27711/USA
Tel. (919)541-5467

Kenneth L. Demerjian
Atmospheric Sciences Research Centre
State University of New York
100 Fuller Road
Albany, NY 12205/USA
Tel. (518)442-3820

Richard G. Derwent
Harwell Laboratories
Didcot, Oxfordshire
OX11 ORA/UK
Tel. (235)24141 ext. 4403

Basil Dimitriades
Atmospheric Sciences Research Laboratory
US Environmental Protection Agency
Research Triangle Park, NC 27711/USA
Tel. (919)541-2706

Ralph Drauschke
Amt für Umweltschutz
Eifelwall 7
5000 Köln/FRG
Tel. (221)2217617

Adolf Ebel
Universität Köln
Institut für Geophysik
und Meteorologie
Albertus Magnus Platz
5000 Köln 41/FRG
Tel. (221)212995

Wolfgang Fricke
Umweltbundesamt
Pilotstation
Frankfurterstr. 135
6050 Offenbach/FRG
Tel. (69)888038

Klaus D. Höfken
GSF München/Projektträger
Umwelt - und Klimaforschung
Ingolstädter Landstr. 1
8042 Neuherberg/FRG
Tel. (89)3187-3375

Harvey E. Jeffries
School of Public Health
University of North Carolina
Chapel Hill, NC 27514/USA
Tel. (919)966-3848

Dieter Jost
Umweltbundesamt
Bismarckplatz 1
1000 Berlin 33/FRG
Tel. (30)8903294

Michael Kaup
Amt für Umweltschutz Köln
Eifelwall 7
5000 Köln/FRG
Tel. (221)2217617

J. Alister Kerr
Department of Chemistry
University of Birmingham
Birmingham B15 2TT/UK
Tel. (21)414-4418

Robert C. Kessler
Systems Applications, Inc.
101 Lucas Valley Road
San Rafael, CA 94903/USA
Tel. (415)472-4011

Dieter Kley
Kernforschungsanlage Jülich
Institut "Chemie der Atmosphäre"
Postfach 1913
5170 Jülich/FRG
Tel. (2461)613741

Barbara Lübkert
OECD, Environment Directorate
2, rue André Pascal
75775 Paris Cedex 16/F
Tel. (1) 45027612 (OECD)
(43-2236)71521547 (IIASA/Austria)

Terry McGuire
Technical Support Division
California Air Resources Board
P.O. Box 2815
Sacramento, CA 95812/USA
Tel. (916)322-5350

Edwin L. Meyer
Office of Air Quality Planning Planning and Standards
US Environmental Protection Agency
Research Triangle Park, NC 27711/USA
Tel. (919)541-5594

Christa Morawa
Umweltbundesamt
Bismarckplatz 1
1000 Berlin 33/FRG
Tel. (30)8903-249

Katrin Nodop
NILU, Norsk Institutt for
Luftforskning
Postboks 64
2001 Lillestrom/N
Tel. (6)814170

Andreas Obermeier
Institut für Kernenergetik
Universität Stuttgart/FRG
Pfaffenwaldring 31
7000 Stuttgart 80
Tel. (711)685-2388

Dieter Paffrath
DRVLR, Institut für
Physik der Atmosphäre"
Münchener Str.
8031 Oberpfaffenhofen/FRG
Tel. (8153)28-511

Jürgen Pankrath
Umweltbundesamt
Bismarckplatz 1
1000 Berlin 33/FRG
Tel. (30)8903-375

Ulrich Platt
Kernforschungsanlage Jülich
ICH 3
Postfach 1913
5170 Jülich/FRG
Tel. (2461)613239

S. Trivikrama Rao
Bureau of Air Research
Division of Air Resources
New York State Department of
Environmental Conservation
50 Wolf Road
Albany, NY 12233/USA
Tel. (518)457-3200

Kenneth L. Schere
Atmospheric Sciences Research Laboratory
US Environmental Protection Agency
Research Triangle Park, NC 27711/USA
Tel. (919)541-3795

Ulrich Schurath
Institut für Phys. Chemie
der Universität Bonn
Wegelerstr. 12
5300 Bonn/FRG
Tel. (228)732507

Rainer Stern
Inst. f. Geophysikalische
Wissenschaften der
Freien Universität Berlin
Thielallee 50
1000 Berlin 33/FRG
Tel. (30)838-3471

David Strother
Office of International Activities
US Environmental Protection Agency
Washington, DC 20460/USA
Tel. (202)382-4892

William Sylte
California Air Resources Board
P.O. Box 2815
Sacramento, CA 95812/USA
Tel. (916)362-9920

Neil B.A. Trivett
Air Quality and Inter-Environment
Research Branch
Atmospheric Environment Service
4905 Dufferin Street
Downsview
Ontario M3H 5T4/Canada
Tel. (416)739-4447

Chris Veldt
TNO
Division of Technology for Society
P.B. 342
NL - 7300 AH Apeldoorn/NL

Harry M. Walker
H.M. Walker and Associates, Inc.
3321 East Bayou Drive
Dickinson, TX 77539/USA
Tel. (713)337-1177

Erich Weber
Bundesministerium für Umwelt,
Naturschutz und Reaktorsicherheit
IG I 2
Postfach
5300 Bonn/FRG
Tel. (228)3052421

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